

- **CHEMICAL KINETICS**
- **RADIOACTIVITY**
- **THERMODYNAMICS**
- **THERMOCHEMISTRY**

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THEORY AND EXERCISE BOOKLET

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JEE SYLLABUS

• CHEMICAL KINETICS

JEE - ADVANCED

Rates of chemical reactions; Order of reactions; Rate constant; First order reactions; Temperature dependence of rate constant (Arrhenius equation).

• RADIOACTIVITY

JEE - ADVANCED

Nuclear chemistry: Radioactivity: isotopes and isobars; Properties of α , β and γ rays; Kinetics of radioactive decay (decay series excluded), carbon dating; Stability of nuclei with respect to proton-neutron ratio; Brief discussion on fission and fusion reactions.

• THERMODYNAMICS

JEE - ADVANCED

Energetics: First law of thermodynamics; Internal energy, work and heat, pressure-volume work; Enthalpy, Hess's law; Heat of reaction, fusion and vapourization; Second law of thermodynamics; Entropy; Free energy; Criterion of spontaneity.

• THERMOCHEMISTRY

JEE - ADVANCED

Internal energy, work and heat, Enthalpy, Hess's law; Heat of reaction, fusion and vapourization;

CHEMICAL KINETICS

This branch of chemistry which deals with the study of rates of chemical reactions and the mechanism by which they occur. While studying reaction, one deals with :

- (a) how fast (or slow) the reactants get converted into products
- (b) the steps or paths through which the products are formed (reaction mechanism)

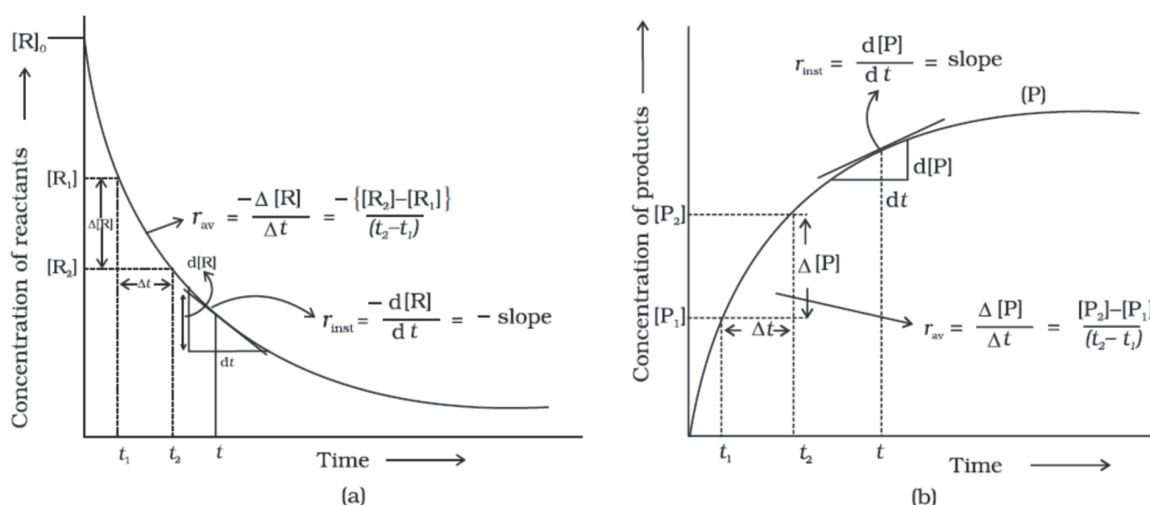
Chemical reaction kinetics deals with the rates of chemical processes. Any chemical process may be broken down into a sequence of one or more single-step processes known either as *elementary processes*, *elementary reactions*, or *elementary steps*. Elementary reactions usually involve either a single reactive collision between two molecules, which we refer to as a *bimolecular* step, or dissociation/isomerisation of a single reactant molecule, which we refer to as a *unimolecular* step. Very rarely, under conditions of extremely high pressure, a *termolecular* step may occur, which involves simultaneous collision of three reactant molecules. An important point to recognise is that many reactions that are written as a single reaction equation in actual fact consist of a series of elementary steps. This will become extremely important as we learn more about the theory of chemical reaction rates.

As a general rule, elementary processes involve a transition between two atomic or molecular states separated by a potential barrier. The potential barrier constitutes the *activation energy* of the process, and determines the rate at which it occurs. When the barrier is low, the thermal energy of the reactants will generally be high enough to surmount the barrier and move over to products, and the reaction will be fast. However, when the barrier is high, only a few reactants will have sufficient energy, and the reaction will be much slower. The presence of a potential barrier to reaction is also the source of the temperature dependence of reaction rates. The huge variety of chemical species, types of reaction, and the accompanying potential energy surfaces involved means that the timescale over which chemical reactions occur covers many orders of magnitude, from very slow reactions, such as iron rusting, to extremely fast reactions, such as the electron transfer processes involved in many biological systems or the combustion reactions occurring in flames. A study into the kinetics of a chemical reaction is usually carried out with one or both of two main goals in mind:

1. Analysis of the sequence of elementary steps giving rise to the overall reaction. i.e. the *reaction mechanism*.
2. Determination of the absolute rate of the reaction and/or its individual elementary steps.

RATE OF A REACTION

In general, for a reaction : $R \rightarrow P$, the behaviour of the concentration of the reactant and product, as the reaction proceeds is shown graphically



From the graph, it is clear that the concentration of the reactant decreases and that of the product increases as the reaction proceeds and the rate of the change of the concentration of the reactant as well as that of the product is also changing.

Rate of a reaction can, now, be defined in two ways :

Average Rate of reaction (r_{av}) given by for the reaction $R \rightarrow P$:

$$r_{av} = -\frac{\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t}$$

where $\Delta[R]$ and $\Delta[P]$ represents the change in the concentrations of 'R' and 'P' respectively over a time interval Δt

The average rate of the reaction between a time interval ($t_f - t_i = \Delta t$) can be determined from the above graph by locating the concentration of 'R' or 'P' on this graph at the time instants t_f and t_i as shown.

If $[R]_f$ and $[R]_i$ are the concentrations of the reactant 'A' at the time instants t_f and t_i then :

$$r_{av} = -\left(\frac{[R]_f - [R]_i}{t_f - t_i}\right)$$

Similarly from the plot of 'P' as a function of 't', we have : $r_{av} = \left(\frac{[P]_f - [P]_i}{t_f - t_i}\right)$

Note :

➤ The above expression for r_{av} is equivalent to the slope of the line joining the points ($t_f, [A]_f$) and ($t_i, [R]_i$) or ($t_f, [P]_f$) and ($t_i, [P]_i$) as shown.

Instantaneous Rate of reaction ($r_{inst.}$) can be calculated from r_{av}

in the limit $\Delta t \rightarrow 0$ and is represented as :

$$r_{inst.} = -\frac{d[R]}{dt} = \frac{d[P]}{dt}$$

Note : ➤ The above expression for $r_{inst.}$ is equivalent to the slope of the tangent from the plot of the concentration of 'R' or 'P' at any time instant 't'.

➤ The rate of the reaction ($r_{inst.}$ or r_{av}) is always calculated as a positive quantity.

➤ The rate of a reaction at any temperature depends on the concentration of the reactants and sometimes on the concentration of some foreign substances (e.g a catalyst) being used in the reaction as well. The representation of this dependence of the rate of the reaction on the concentrations is known as **rate law** and this rate law is determined experimentally.

Units of rate of a reaction

Units of rate are concentration time⁻¹. For example, if concentration is in mol L⁻¹ and time is in seconds then the units will be mol L⁻¹s⁻¹. However, in gaseous reactions, when the concentration of gas is expressed in terms of their partial pressures, then the units of the rate equation will be atm s⁻¹.

Relation between various rates :

In general for a reaction : $aA + bB \rightarrow cC + dD$

The rate of reaction can be expressed as follows :

$$\text{Rate} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = +\frac{1}{c} \frac{d[C]}{dt} = +\frac{1}{d} \frac{d[D]}{dt} = k_r[A]^m[B]^n$$

ORDER OF A REACTION

By performing a reaction in actual in laboratory and carefully examining it, it is possible to express the rate law as the product of concentrations of reactants each raised to some power. For example consider the reaction : $aA + bB \rightarrow cC + dD$. The differential rate law is written as :

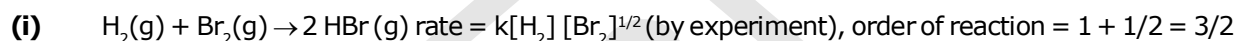
$$\text{Rate} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = +\frac{1}{c} \frac{d[C]}{dt} = +\frac{1}{d} \frac{d[D]}{dt} = k_r[A]^m[B]^n$$

where k_r is called as **rate constant of the reaction** or **velocity constant** or **specific reaction rate**. k is a characteristic of a reaction at a given temperature. It changing only when the temperature changes.

The powers m and n are integers or fractions. m is called as order of reaction with respect to A and n is called as order of reaction with respect to B. The overall order of reaction = $m + n$

Hence, the sum of powers of the concentration of the reactants in the rate law expression is called the order of that chemical reaction.

- The values of m and n are calculated from the experimental data obtained for a reaction and the powers m and n are not related to the stoichiometric coefficients of the reactants
- Order can be fractional, zero or negative.
For example consider the following reaction :

**Units of k :**

In general, the rate law for a n^{th} order reaction can be taken as : $\frac{dc}{dt} = -kc^n$

where k : rate constant; c : concentration and n : order of reaction

$$\Rightarrow k = \frac{dc/dt}{c^n} \Rightarrow \text{Units of } k \equiv (\text{mol/L})^{1-n} (\text{time})^{-1}$$

For a 'zero' order reaction ($n = 0$) : Units of $k = (\text{mol/L})^1 (\text{time})^{-1}$ or mol/L/sec

For a first order reaction ($n = 1$) : Units of $k \equiv (\text{time})^{-1}$ e.g. sec^{-1} , min^{-1} , hrs^{-1} etc.

For a second order reaction ($n = 2$) : Units of $k \equiv (\text{mol/L})^{-1} (\text{time})^{-1}$ or L/mol/sec .

MOLECULARITY

As already discussed, the order of a reaction is an experimental concept.

A complex chemical reaction is understood in terms of various indirect steps called elementary processes. The study of a reaction in terms of elementary processes is called as reaction mechanism. Now various elementary steps occur at different rates.

The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction.

In the rate determining step, when one molecule takes part, it is said to be a unimolecular reaction ; two molecules take part, it is said to be a bimolecular reaction; three molecules take part, it is said to be a termolecular reaction.

Unimolecular :

1. Cyclopropane \rightarrow propene
2. $\text{O}_3(\text{g}) \rightarrow \text{O}_2(\text{g}) + \text{O}(\text{g})$
3. $\text{N}_2\text{O}_5(\text{g}) \rightarrow \text{N}_2\text{O}_4(\text{g}) + 1/2\text{O}_2(\text{g})$

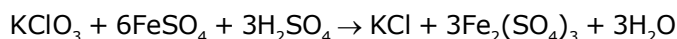
Bimolecular :

1. $\text{NO}(\text{g}) + \text{O}_3(\text{g}) \rightarrow \text{NO}_2(\text{g}) + \text{O}_2(\text{g})$
2. $2\text{HI}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$

Termolecular :

1. $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$

The probability that more than three molecules can collide and react simultaneously is very small. Hence, reactions with the molecularity three are very rare and slow to proceed. It is, therefore, evident that complex reactions involving more than three molecules in the stoichiometric equation must take place in more than one step.



This reaction which apparently seems to be of tenth order is actually a second order reaction. This shows that this reaction takes place in several steps. Which step controls the rate of the overall reaction? The question can be answered if we go through the mechanism of reaction, for example, chances to win the relay race competition by a team depend upon the slowest person in the team. Similarly, the overall rate of the reaction is controlled by the slowest step in a reaction called the rate determining step.

(i) Order of a reaction is an experimental quantity. It can be zero and even a fraction but molecularity cannot be zero or a non integer.

(ii) Order is applicable to elementary as well as complex reactions whereas molecularity is applicable only for elementary reactions. For complex reaction molecularity has no meaning. 103 Chemical Kinetics

(iii) For complex reaction, order is given by the slowest step and molecularity of the slowest step is same as the order of the overall reaction.

➤ For a reaction : $\text{A} \rightarrow \text{B}$ in the rate law : $\text{rate} = k[\text{A}]^m [\text{B}]^n$

Neither the order of reaction ($m + n$) nor the molecularity of a reaction can be predicted from stoichiometric coefficient of a balanced reaction. The order of reaction is always to be determined experimentally and molecularity is determined theoretically after studying the reaction mechanism. However as a theoretical idea sometime, we can have an approximate order of reaction equal to molecularity (i.e., the number of molecules taking part in slowest elementary for complex reactions).

Problem 1 :

The rate of formation of $\text{NO}(\text{g})$ in the reaction $\text{NOBr}(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{Br}_2(\text{g})$ is found to be $1.6 \times 10^{-4} \text{ M/s}$. Find the rate of overall reaction rate and rate of consumption of NOBr .

We have : $\frac{d[\text{NO}]}{dt} = 1.6 \times 10^{-4} \text{ M/s}$.

First write a balanced chemical equation. $2\text{NOBr}(\text{g}) \rightarrow 2\text{NO}(\text{g}) + \text{Br}_2(\text{g})$

Now, Rate of overall reaction = $-\frac{1}{2} \frac{d[\text{NOBr}]}{dt} = +\frac{1}{2} \frac{d[\text{NO}]}{dt} = \frac{1}{1} \frac{d[\text{Br}_2]}{dt} = 0.8 \times 10^{-4} \text{ M/s}$

Rate of consumption of $\text{NOBr} = -\frac{d[\text{NOBr}]}{dt} = +1.6 \times 10^{-4} \text{ M/s}$

Problem 2 :

The rate constant for a given reaction is $k = 3 \times 10^{-5} \text{ s}^{-1} \text{ atm}^{-1}$. Express it in units of $\text{L mol}^{-1} \text{ sec}^{-1}$.

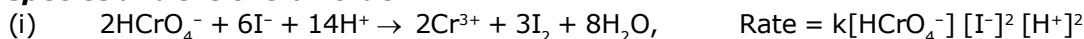
Sol. $PV = nRT \Rightarrow P = cRT$ (c : concentration in mol/L)

Substitute $R = 0.0821 \text{ L-atm/mol/K}$; $T = 273 \text{ K}$; $P = 1 \text{ atm} \Rightarrow c = 0.04462 \text{ mol/L}$

$$\Rightarrow k = \frac{3 \times 10^{-5}}{0.04462} = 6.73 \times 10^{-4} \text{ L/mol/s.}$$

Problem 3 :

From the rate laws for the reactions given below, determine the order with respect to each species and the overall order :



Sol. (i) The order of the reaction with respect to $[\text{HCrO}_4^-]$ is 1; with respect to $[\text{I}^-]$ is 2 and with respect to $[\text{H}^+]$ is 2. The overall order of the reaction is $1 + 2 + 2 = 5$

(ii) The order of the reaction with respect to $[\text{H}_2\text{O}_2]$ is 1 and with respect to $[\text{I}^-]$ is 1. The overall order of the reaction is $1 + 1 = 2$.

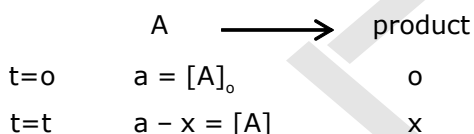
➤ In (i) stoichiometric coefficient of I^- is 6 whereas the power coefficient (n) in the rate law is 2.

➤ Reaction (i) may not take place in a single step. It may not be possible for all the 22 molecules to be in a state to collide with each other simultaneously. Such a reaction is called a complex reaction.

➤ A complex reaction takes place in a series of a number of elementary reactions.

Zero Order Reactions :

The rate law for zero order reactions ($n = 0$) is written as :



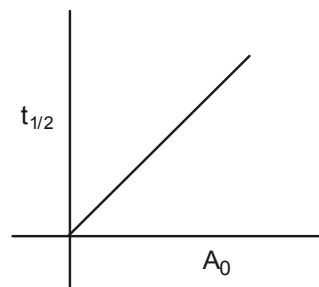
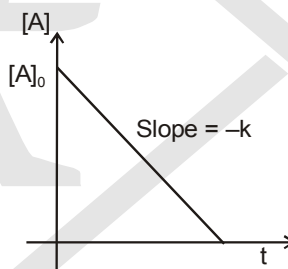
$$-\frac{d[\text{A}]}{dt} = k[\text{A}]^0$$

$$-\frac{d[\text{A}]}{dt} = k$$

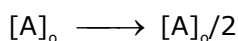
$$-\int_{[\text{A}]_0}^{[\text{A}]} d[\text{A}] = k \int_0^t dt$$

$$[\text{A}]_0 - [\text{A}] = kt$$

$$k = \frac{[\text{A}]_0 - [\text{A}]}{t} = \frac{x}{t}$$

★ **Half life ($t_{1/2}$) :**

Time in which half of initial amount is left.

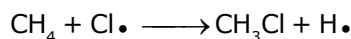
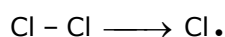
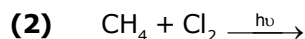


$$t = 0 \quad t = t_{1/2}$$

$$k = \frac{[\text{A}]_0 - [\text{A}]_0/2}{t_{1/2}}$$

$$t_{1/2} = \frac{[\text{A}]_0}{2k}$$

Thus, for a Zero order reaction, half life is directly proportional to initial concentration of the reactant. Clearly, zero order reactions are those, whose rates are not affected by change in concentrations of reactants (i.e., independent of concentration). The rates of such reactions only depend upon temperature. Most of photochemical reactions are zero order reactions. Other examples are : decomposition of HI over the surface of gold and NH_3 over tungsten.

Example :**(1)** Photochemical Reactions, Photosynthesis**FIRST ORDER REACTION**

$t = 0 \quad [\text{A}]_0$

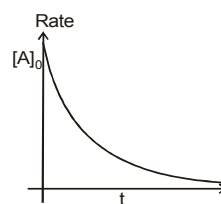
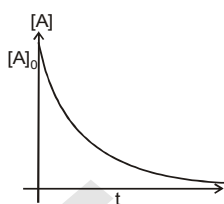
$t = t \quad [\text{A}] \quad [\text{P}]$

$$-\frac{d[\text{A}]}{dt} = k[\text{A}]$$

$$-\int_{[\text{A}]_0}^{[\text{A}]} \frac{d[\text{A}]}{[\text{A}]} = k \int_0^t dt$$

$$\ln [\text{A}]_0 / [\text{A}] = kt$$

$$k = \frac{2.303}{t} \log \frac{[\text{A}]_0}{[\text{A}]}$$

★ **Half life ($t_{1/2}$) :**

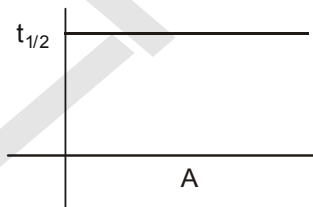
$$t = t_{1/2} \quad [\text{A}] = [\text{A}]_0 / 2$$

$$k = \frac{2.303}{t_{1/2}} \log \frac{[\text{A}]_0}{[\text{A}]_0 / 2} = \frac{2.303}{t_{1/2}} \log 2$$

$$t_{1/2} = \frac{2.303}{k} \log_{10} 2$$

$$t_{1/2} = \frac{0.693}{k}$$

$$t_{1/2} = \frac{\log_e 2}{k}$$



$$[\text{A}] = \frac{[\text{A}]_0}{2^n} \quad \text{where } n = \text{number of half lifes.}$$

★ **Average life :**

$$t_{av} = 1.44 \quad t_{1/2} = \frac{1}{k}$$

Features of a First Order Reaction :

1. A first order reaction must follow above form of rate law for all time instants. This means if we are given value of A_0 and values of x at different time instants [i.e. ($A_0 - x$) as value of reactants after t], the values of k can be calculated for different time instants by using the above first order law. If the reaction for which the data were given is a first order reaction, then all values of k will approximately equal to each other.

2. **The time for half reaction for a first order reaction is independent of initial concentration of reactants.**

3. The concentration of reactants in a first order reaction decreases exponentially with time (see figure)
Note that plot of $\log_{10} A$ vs t is linear.

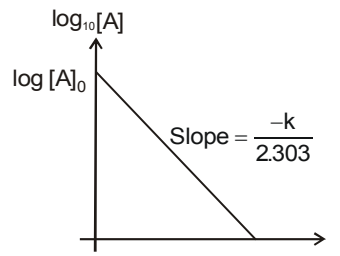
Example :

(1) Radioactive disintegration.

(2) $\text{PCl}_5(\text{g}) \longrightarrow \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$

(3) $\text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \frac{1}{2}\text{O}_2$

(4) $\text{NH}_4\text{NO}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$



➤ **Rate constant of a first order reaction can also be calculated by measuring the concentration of the reactants at two time instants (if the initial concentration is not known).**

If A_1 and A_2 are the reactant's concentrations at two time instants ' t_1 ' and ' t_2 ' respectively, then we have :

$$2.303 \log_{10} \frac{A_0}{A_1} = kt_1 \quad \dots \text{(iii)} \quad \text{and} \quad 2.303 \log_{10} \frac{A_0}{A_2} = kt_2 \quad \dots \text{(iv)}$$

Subtracting (iv) from (iii), we get :

$$2.303 \log_{10} \frac{A_1}{A_2} = k(t_1 - t_2) \quad \text{Thus, } k \text{ can be evaluated.}$$

Problem : 4

For a reaction $2\text{NO}(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$; the following data were obtained.

	$[\text{NO}] (\text{mol/L})$	$[\text{H}_2] (\text{mol/L})$	Rate (mol/L/s)
1.	5×10^{-3}	2.5×10^{-3}	3×10^{-5}
2.	15×10^{-3}	2.5×10^{-3}	9×10^{-5}
3.	15×10^{-3}	10×10^{-3}	3.6×10^{-4}

(a) **Calculate the order of reaction.**

(b) **Find the rate constant.**

(c) **Find the initial rate if $[\text{NO}] = [\text{H}_2] = 8.0 \times 10^{-3} \text{ M}$**

Assuming rate law can be expressed as follows :

$$\text{rate} = k[\text{NO}]^x [\text{H}_2]^y$$

By analysing the data :

From observation 1 and 2, we see that $[\text{H}_2]$ is constant and when $[\text{NO}]$ is tripled, the rate is also tripled.

$$\Rightarrow \text{rate (r)} \propto [\text{NO}] \quad \Rightarrow \quad x = 1$$

From observations 2 and 3, we see that $[\text{NO}]$ is constant; when $[\text{H}_2]$ is increased four times, the rate also increases four times :

$$\text{rate} \propto [\text{H}_2] \quad \Rightarrow \quad y = 1$$

$$\Rightarrow r = k[\text{NO}][\text{H}_2\text{O}]$$

\Rightarrow The order of reaction w.r.t No and H_2 is 1 and the overall order of reaction is $1 + 1 = 2$.

$$\text{Initial rate} = k[\text{NO}][\text{H}_2] = 2.4 \times (8 \times 10^{-3})^2 = 1.536 \times 10^{-4} \text{ mol/L/s.}$$

Second Order kinetics

★ **Case I :** $A \longrightarrow \text{product}$

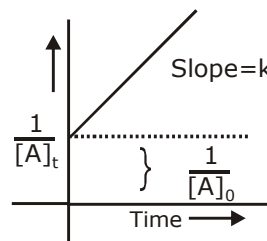
$$\begin{array}{lll} t = 0 & [A]_0 & - \\ t = t & [A]_t & [P] \end{array}$$

$$-\frac{d[A]}{dt} = k[A]^2$$

$$-\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^2} = k \int_0^t dt$$

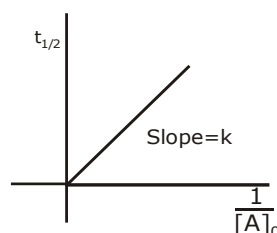
$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

$$k = \frac{1/[A] - 1/[A]_0}{t}$$



★ **Half-life ($t_{1/2}$) :** $[A]_t = \frac{[A]_0}{2}, k = 2/[A]_0 - 1/[A]_0$

$$t_{1/2} = \frac{1}{k[A]_0}$$

**Example :**

(1) Alkaline hydrolysis of esters.

(2) Self Cannizzaro's reactions,

★ **Case (II):**



$$\begin{array}{lll} t = 0 & a & b \\ t = t & a-x & b-x \end{array}$$

$$-\frac{d[A]}{dt} = k[A][B], \quad \frac{dx}{dt} = k(a-x)(b-x)$$

$$\int_0^x \frac{dx}{(a-x)(b-x)} = k \int_0^t dt, \quad \int_0^x \frac{dx}{(b-a)(a-x)} + \int_0^x \frac{dx}{(a-b)(b-x)} = k \int_0^t dt$$

$$\frac{(-1)}{(b-a)} \ln \left(\frac{a-x}{a} \right) + \frac{(-1)}{(a-b)} \ln \left(\frac{b-x}{b} \right) = kt$$

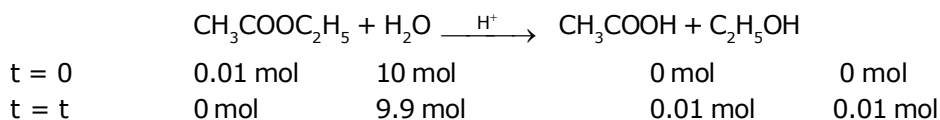
$$\ln \frac{a}{a-x} - \ln \frac{b}{b-x} = k(b-a)t$$

$$k = \frac{1}{t(b-a)} \left[\ln \left(\frac{a}{a-x} \times \frac{b-x}{b} \right) \right]$$

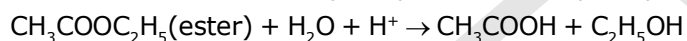
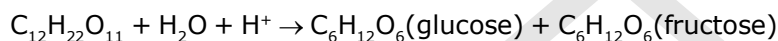
$$k = \frac{1}{t(b-a)} \ln \frac{a(b-x)}{b(a-x)}$$

Pseudo First Order Reaction

The order of a reaction is sometimes altered by conditions. Consider a chemical reaction between two substances when one reactant is present in large excess. During the hydrolysis of 0.01 mol of ethyl acetate with 10 mol of water, amounts of the various constituents at the beginning ($t = 0$) and completion (t) of the reaction are given as under.



The concentration of water does not get altered much during the course of the reaction. So, in the rate equation $\text{Rate} = k'[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]$ the term $[\text{H}_2\text{O}]$ can be taken as constant. The equation, thus, becomes $\text{Rate} = k[\text{CH}_3\text{COOC}_2\text{H}_5]$ where $k = k'[\text{H}_2\text{O}]$ and the reaction behaves as first order reaction. The molecularity of acidic hydrolysis of sucrose and esters is 2, whereas their order is 1. In both the reactions water is in excess so that its concentration remains constant throughout the reaction. The rate of reaction therefore depends only on the concentration of sucrose and ester in two reactions respectively. So the reactions in which the molecularity is 2 or 3 but they conform to the first order kinetics are known as pseudo first order reactions OR pseudo unimolecular reactions.



(In both the reactions, H^+ ion acts as a catalyst)

n^{TH} ORDER KINETICS



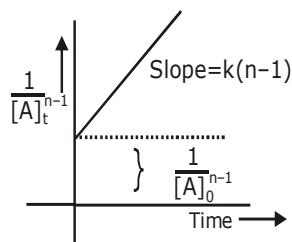
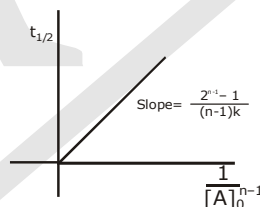
$$-\frac{d[A]}{dt} = k[A]^n$$

$$-\int_{[A]_0}^{[A]} \frac{d[A]}{[A]^n} = k \int_0^t dt$$

$$\frac{1}{(n-1)} \left[\frac{1}{[A]^{n-1}} \right]_{[A]_0}^{[A]} = kt$$

$$\frac{1}{(n-1)} \left[\frac{1}{[A]_t^{n-1}} - \frac{1}{[A]_0^{n-1}} \right] = kt$$

$$k = \frac{1}{(n-1)t} \left[\frac{1}{[A]_t^{n-1}} - \frac{1}{[A]_0^{n-1}} \right]$$



★ **Half-life ($t_{1/2}$) :** at $t = t_{1/2}$, $[A]_t = \frac{[A]_0}{2}$

$$\Rightarrow k = \frac{1}{(n-1)t_{1/2}} \left[\frac{2^{n-1}}{[A]_0^{n-1}} - \frac{1}{[A]_0^{n-1}} \right]$$

$$\Rightarrow t_{1/2} = \frac{2^{n-1} - 1}{(n-1)k[A]_0^{n-1}} \Rightarrow t_{1/2} \propto \frac{1}{[A]_0^{n-1}}$$

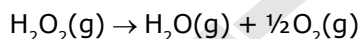
Problem : 5

For the non-equilibrium process, $A + B \rightarrow \text{Products}$, the rate is first order w.r.t A and second order w.r.t B. If 1.0 mole each of A and B are introduced into a 1 litre vessel and the initial rate were 1.0×10^{-2} mol/litre-sec, calculate the rate when half of the reactants have been used.

Sol. Rate = $K[A][B]^2$
 $\therefore 10^{-2} = K[1][1]^2$
 or $K = 10^{-2} \text{ litre}^2 \text{ mol}^{-2} \text{ sec}^{-1}$
 Now rate_{II} = $10^{-2} \times 0.5 \times (0.5)^2$
 or New rate = **$1.2 \times 10^{-3} \text{ mol/L-sec}$**

ANALYSIS OF SOME IMPORTANT FIRST-ORDER REACTIONS

Decomposition of Hydrogen peroxide (H_2O_2)



The rate of this first order reaction is measured by titrating a fixed volume of H_2O_2 (undecomposed) against a standard solution of KMnO_4 . Here KMnO_4 acts as oxidising agent and H_2O_2 as reducing agent. The volumes of KMnO_4 used for H_2O_2 after regular intervals of time are as follows.

Time instants	$t = 0$	t_1	t_2	t_3	t_4	t_5
Vol. of KMnO_4	V_0	V_1	V_2	V_3	V_4	V_5

Volume of KMnO_4 at $t = 0$ corresponds to volume of H_2O_2 initially present.

$$\Rightarrow A_0 \propto V_0$$

Volume of KMnO_4 at time instants t_1, t_2, t_3, \dots corresponds to volume of H_2O_2 remaining after

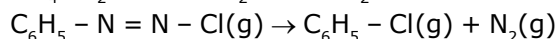
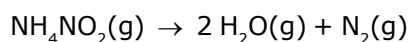
t_1, t_2, t_3, \dots

$$\Rightarrow A \propto V_t$$

Now it being a first order reaction, follows first order kinetics, so

$$k t = 2.303 \log_{10} \frac{V_0}{V_t}$$

Now using the above expression, if we calculate the values of k for different time intervals t_1, t_2, \dots (for actual numerical data), the values of k should be same if the reaction follows first order kinetics.

Decomposition of ammonium nitrite (NH_4NO_2)**and benzene diazonium chloride ($\text{C}_6\text{H}_5\text{N} = \text{NCl}$)**

The rate of both the reaction is studied (measured) in similar manner. The volume of nitrogen (N_2) is collected after a regular interval of time as follows :

Time instants	$t = 0$	t_1	t_2	t_3	t_4	t
Vol. of N_2	0	V_1	V_2	V_3	V_4	V_∞

At $t = 0$, clearly the volume of $\text{N}_2 = 0$

Time instant $t = \infty$ means the end of a reaction i.e., when whole of NH_4NO_2 or $\text{C}_6\text{H}_5 - \text{N} = \text{N} - \text{Cl}$ is decomposed.

⇒ At $t = \infty$, V_∞ corresponds to the initial volume of NH_4NO_2 or $\text{C}_6\text{H}_5 - \text{N} = \text{N} - \text{Cl}$

(Note that the ratio of stoichiometric coefficient for both N_2 : NH_4NO_2 or N_2 : $\text{C}_6\text{H}_5\text{N} = \text{NCl}$ is 1 : 1)

⇒ $A_0 \propto V_\infty$

At $t = t_1, t_2, t_3, \dots$ the volume of N_2 corresponds to concentration of product formed i.e., equal to x .

⇒ $x \propto V_t$

⇒ $A_0 - x \propto V_\infty - V_t$

⇒ $kt = 2.303 \log_{10} \frac{V_\infty}{V_\infty - V_t}$

Hydrolysis of Esters ($\text{CH}_3\text{COOC}_2\text{H}_5$)

The reaction rate is measured by titrating the acid (CH_3COOH) produced against a standard alkali solution. Note that when a test sample is prepared from the reacting mixture, there are two acids : one is mineral acid H^+ (HCl or any other) and second is CH_3COOH produced. So volume of alkali used gives titration value for both acids. The data is collected in the following manner.

Time instants	$t = 0$	t_1	t_2	t_3	t_4	t_∞
Vol. of NaOH	V_0	V_1	V_2	V_3	V_4	V_∞

At $t = 0$, V_0 is the volume NaOH used to neutralise the mineral acid present (H^+) being used as catalyst. (At $t = 0$, no CH_3COOH is yet produced)

At $t = \infty$ (i.e., at the end of hydrolysis), V_∞ is the volume of NaOH used to neutralise whole of CH_3COOH plus vol. of HCl present. At $t = \infty$, volume of CH_3COOH corresponds to volume of ester taken initially

⇒ $A_0 \propto V_\infty - V_0$ (as $V_0 \equiv$ vol. of HCl)

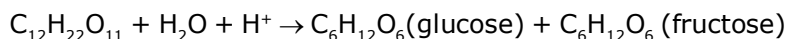
At $t = t_1, t_2, t_3, \dots$ V_1, V_2, V_3, \dots corresponds to vol. of HCl plus vol. of CH_3COOH being produced.

⇒ $x \propto V_t - V_0$

⇒ $A_0 - x \propto (V_\infty - V_0) - (V_t - V_0)$

⇒ $A_0 - x \propto V_\infty - V_t$

⇒ $kt = 2.303 \log_{10} \frac{V_\infty - V_0}{V_\infty - V_t}$

Inversion of Cane Sugar ($C_{12}H_{22}O_{11}$)

The rate is measured by measuring the change in the angle of rotation (optical activity) by a polarimeter. Sucrose is dextro-rotatory, glucose is dextro-rotatory and fructose is leavo-rotatory. The change produced in rotatory power in time t gives a measure of x , the quantity of sucrose decomposed in that time. The total change in the rotatory power produced at the end of the reaction gives the measure of A_0 , the initial concentration of sucrose.

If r_0 , r_t and r_∞ represent rotations at the start of reaction, after time t and at the end of reaction respectively, then

$$\Rightarrow A_0 \propto r_0 - r_\infty \quad \text{and} \quad x \propto r_0 - r_t$$

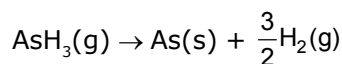
$$\Rightarrow A_0 - x \propto r_t - r_\infty$$

$$\Rightarrow kt = 2.303 \log_{10} \frac{r_0 - r_\infty}{r_t - r_\infty}$$

DECOMPOSITION OF $AsH_3(g)$

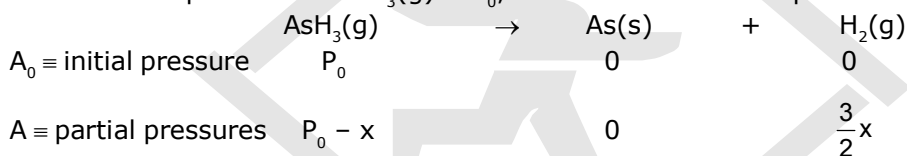
In first-order reactions involving gases, sometime measuring the pressure of the reaction mixture is very good method for measuring reaction rates.

For example consider decomposition of arsine gas (AsH_3)



The rate of reaction is measured as the *increase* in pressure of the reaction mixture. Note that there is an increase in number of moles of the gaseous products to the right, so as the reaction proceeds, there will be an increase in pressure of contents ($P \propto n$).

Let the initial pressure of $AsH_3(g)$ is P_0 , if x is the decrease in pressure of $AsH_3(g)$ after time t .



Arsenic is solid, so $P(As) = 0$

After time t , let P_t be the total pressure, then

$$P_t = P(AsH_3) + P(H_2) = (P_0 - x) + \frac{3}{2}x$$

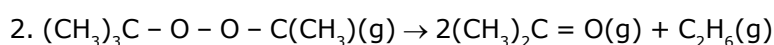
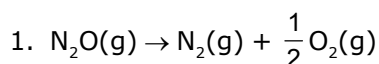
$$\Rightarrow P_t = P_0 + \frac{1}{2}x \quad \Rightarrow \quad x = 2(P_t - P_0)$$

Now $A_0 \propto P_0$

and $A \propto P_0 - x \equiv P_0 - 2(P_t - P_0) \equiv 3P_0 - 2P_t$

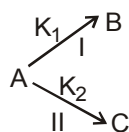
$$\Rightarrow kt = 2.303 \log_{10} \frac{P_0}{3P_0 - 2P_t}$$

On similar pattern, please try to write the expression for 1st order rate law for following first-order reactions. (in terms of P_0 and P_t)



COMPLEX (FIRST ORDER) KINETICS

(A) Parallel Kinetics

Rate of change of A = [rate of change of A]_I + [rate of change of A]_{II}

$$-\frac{d[A]}{dt} = K_1[A] + K_2[A], \quad \frac{dB}{dt} = k_1A, \quad \frac{dC}{dt} = k_2A$$

$$\Rightarrow \frac{[B]}{[C]} = \frac{k_1}{k_2}$$

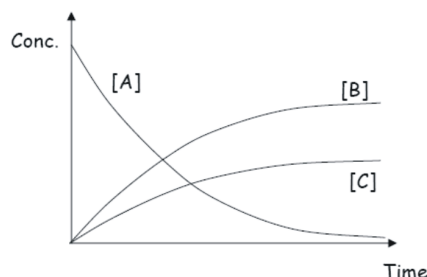
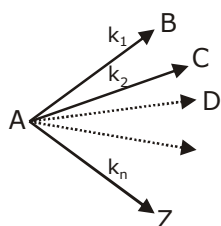
$$\% \text{ of B in the mix of A \& B} = \frac{k_1}{k_1 + k_2} \times 100$$

$$\% \text{ of C in the} = \frac{k_2}{k_1 + k_2} \times 100$$

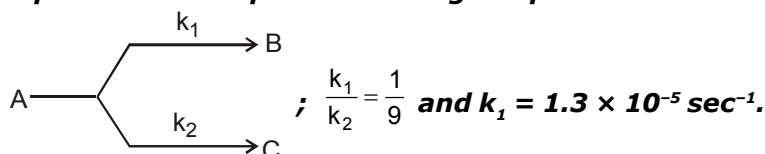
$$-\frac{d[A]}{dt} = (K_1 + K_2)[A]$$

$$K_1 + K_2 = \frac{2.303}{t} \log_{10} \frac{[A]_0}{[A]}$$

$$t_{1/2} = \frac{0.693}{K_1 + K_2}$$

**GENERALIZATION**

$$K_1 + K_2 + \dots + K_n = \frac{2.303}{t} \log \frac{[A]_0}{[A]_t}, \quad t_{1/2} = \frac{0.693}{K_1 + K_2 + \dots + K_n}$$

Problem : 6**An organic compound A decomposes following two parallel first order mechanisms :****Calculate the concentration ratio of C to A, if an experiment is allowed to start with only A for one hour.**

Sol.

$$\frac{k_1}{k_2} = \frac{1}{9}$$

But $k_1 = 1.3 \times 10^{-5} \text{ sec}^{-1}$; $k_2 = 9 \times 1.3 \times 10^{-5} \text{ sec}^{-1} = 117 \times 10^{-5} \text{ sec}^{-1}$
 $(k_1 + k_2) = (1.3 \times 10^{-5}) + (11.7 \times 10^{-5}) \text{ sec}^{-1} = 13 \times 10^{-5} \text{ sec}^{-1} \quad \dots(1)$

Also $\frac{[B]_t}{[C]_t} = \frac{1}{9} \Rightarrow [B]_t = \frac{[C]_t}{9} \quad \dots(2)$

$$\Rightarrow \ln \frac{[A]_0}{[A]_t} = (k_1 + k_2)t ; \ln \left[\frac{[A]_t + [B]_t + [C]_t}{[A]_t} \right] = (k_1 + k_2)t$$

$$\Rightarrow \ln \left[\frac{[A]_t + \frac{[C]_t}{9} + [C]_t}{[A]_t} \right] = (k_1 + k_2)t \quad [\text{from eq. (2)}] \Rightarrow \ln \left[1 + \frac{10}{9} \frac{[C]_t}{[A]_t} \right] = (k_1 + k_2)t$$

$$\Rightarrow \ln \left[1 + \frac{10}{9} \frac{[C]_t}{[A]_t} \right] = 13 \times 10^{-5} \times 60 \times 60 = 0.468 \quad [\text{from eq. (1)}]$$

$$\Rightarrow 1 + \frac{10}{9} \frac{[C]_t}{[A]_t} = 1.5968 ; \frac{[C]_t}{[A]_t} = 0.537$$

(2) SERIES KINETICS



$$-\frac{d[A]}{dt} = k_1 [A],$$

$$[A]_t = [A]_0 e^{-k_1 t}$$

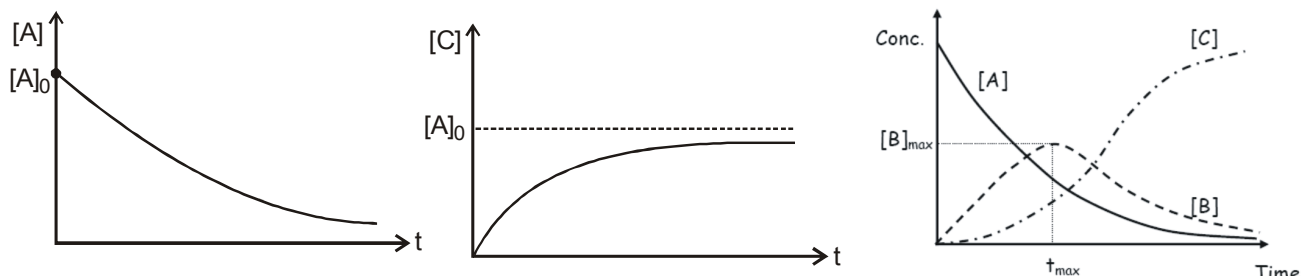
$$\frac{d[B]}{dt} = k_1 [A] - k_2 [B],$$

$$[B] = \frac{k_1 [A]_0}{(k_2 - k_1)} [e^{-k_1 t} - e^{-k_2 t}]$$

$$\frac{d[C]}{dt} = k_2 [B],$$

$$[C] = \frac{k_1 k_2 [A]_0}{k_1 - k_2} \left[\frac{(e^{-k_1 t} - 1)}{k_1} - \frac{(e^{-k_2 t} - 1)}{k_2} \right]$$

★

Graph of [A], [B], [C] Vs t:

Time when [B] is maximum

$$[B] = \frac{k_1[A]_0}{k_2 - k_1} [e^{-k_1 t} - e^{-k_2 t}]$$

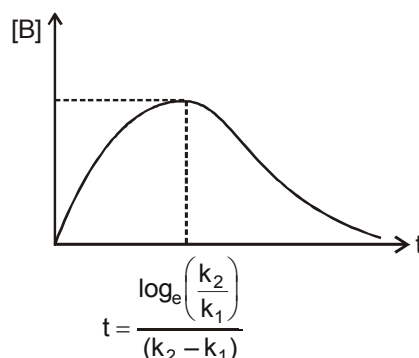
$$\frac{d[B]}{dt} = \frac{k_1[A]_0}{k_2 - k_1} [-k_1 e^{-k_1 t} - (-k_2) e^{-k_2 t}] = 0$$

$$k_1 e^{-k_1 t} = k_2 e^{-k_2 t}$$

$$e^{(k_2 - k_1)t} = \frac{k_2}{k_1}$$

$$(k_2 - k_1)t = \log_e \frac{k_2}{k_1}$$

$$t = \frac{\log_e (k_2/k_1)}{k_2 - k_1}$$

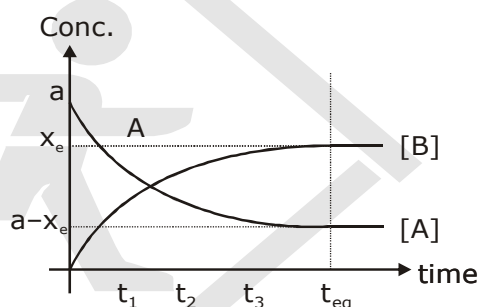


REVERSIBLE KINETICS

★

	A	⇌	B
t = 0	a		0
t = t ₁	a - x ₁		x ₁
t = t ₂	a - x ₂		x ₂
t = t ₃	a - x ₃		x ₃

t = t _{eq}	a - x		x



$0 < t < t_{eq} \longrightarrow$ **CHEMICAL KINETICS**, $t_{eq} \leq t < \infty \longrightarrow$ **CHEMICAL EQUILIBRIUM**

At equilibrium, $r_f = r_b$, $k_1 [A]_{equilibrium} = k_2 [B]_{equilibrium}$, $\frac{k_1}{k_2} = \frac{[B]_{eq.}}{[A]_{eq.}}$

$$\frac{k_1}{k_2} = \frac{[A]_0 - [A]_{equilibrium}}{[A]_{equilibrium}} = \frac{[A]_0}{[A]_{eq}} - 1, \quad \frac{k_1 + k_2}{k_2} = \frac{[A]_0}{[A]_{eq}}$$

$$[A]_{equilibrium} = \frac{k_2 [A]_0}{k_1 + k_2} \dots\dots\dots (I)$$

$$\begin{aligned} \frac{d[A]}{dt} &= -k_1 [A] + k_2 [B], \quad \frac{d[A]}{dt} = -k_1 [A] + k_2 [[A]_0 - [A]] = -(k_1 + k_2) [A] + k_2 [A]_0 \\ &= (k_1 + k_2) \left[-[A] + \frac{k_2}{k_1 + k_2} [A]_0 \right] \end{aligned}$$

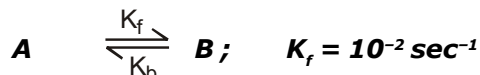
By substituting the value from equation (I)

$$\frac{d[A]}{dt} = (k_1 + k_2)[A]_{eq} - [A] \Rightarrow \int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]_{eq} - [A]} = (k_1 + k_2) \int_0^t dt$$

$$\log_e \frac{[A]_{eq} - [A]_0}{[A]_{eq} - [A]_t} = (k_1 + k_2)t$$

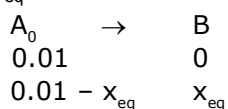
$$(k_1 + k_2) = \frac{2.303}{t} \log_{10} \frac{[A]_{eq} - [A]_0}{[A]_{eq} - [A]_t}$$

Problem : 7 For a reversible first order reaction,



and $\frac{B_{eq}}{A_{eq}} = 4$; If $A_0 = 0.01 \text{ ML}^{-1}$ and $B_0 = 0$, what will be concentration of B after 30 sec ?

Sol.



$$\frac{[B]_{eq}}{[A]_{eq}} = \frac{10^{-2}}{K_b} = 4 = \frac{[x]_{eq}}{0.01 - [x]_{eq}}$$

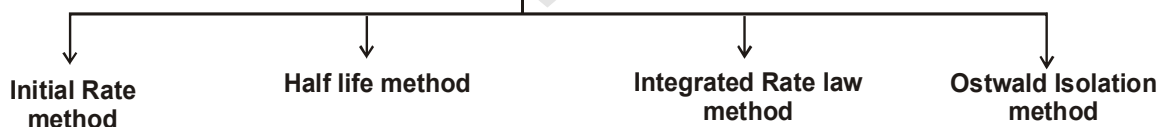
$$\therefore K_b = 0.25 \times 10^{-2} \quad \text{and} \quad x_{eq} = \frac{0.04}{5} = 0.008$$

$$t = \frac{2.303}{(K_f + K_b)} \log \frac{[x]_{eq}}{[x]_{eq} - x}$$

$$30 = \frac{2.303}{1.25 \times 10^{-2}} \log \frac{0.008}{(0.008 - x)}$$

$$\therefore \frac{0.008}{0.008 - x} = 1.455 \quad \therefore x = 2.50 \times 10^{-3}$$

Ways to determine order of reaction



(1) Initial Rate Method



$$\text{rate} = k [A]^m [B]^n; \quad \text{Order} = m + n$$

	[A]	[B]	rate
Experiment 1	0.1	0.1	2×10^{-3}
Experiment 2	0.1	0.2	4×10^{-3}
Experiment 3	0.2	0.1	32×10^{-3}

Experiment (1) and Experiment (2)

$$\frac{2 \times 10^{-3}}{4 \times 10^{-3}} = \frac{k [0.1]^m [0.1]^n}{k [0.1]^m [0.2]^n}$$

$$\left(\frac{1}{2}\right)^1 = \left(\frac{1}{2}\right)^n$$

$$n = 1$$

Experiment (1) and Experiment (3)

$$\frac{2 \times 10^{-3}}{32 \times 10^{-3}} = \frac{k [0.1]^m [0.1]^n}{k [0.2]^m [0.1]^n}$$

$$\left(\frac{1}{2}\right)^4 = \left(\frac{1}{2}\right)^m$$

$$m = 4$$

$$\text{Order } (m + n) = 4 + 1 = 5$$

(2) Half - life method

$t_{1/2}$	$[A]_0$	
1 hr	0.1	$t_{1/2} \propto \frac{1}{[A]^{n-1}}$
2 hr	0.2	

$$\frac{[t_{1/2}]_1}{[t_{1/2}]_2} = \left(\frac{1}{2}\right)^{-1} = \frac{[0.1]^{n-1}}{[0.2]^{n-1}}$$

$$\left(\frac{1}{2}\right)^{-1} = \left(\frac{1}{2}\right)^{n-1}$$

$$n = 0$$

$$n = 1 + \frac{\log (t_{1/2})_2 / (t_{1/2})_1}{\log [A]_{0_1} / [A]_{0_2}}$$

(3) Integrated Rate law Method

A \longrightarrow product

$t = 0$ 1000 M

$t = 60 \text{ sec}$ 100 M

$t = 120 \text{ sec}$ 10 M

$$n = 0 \quad k = \frac{[A]_0 - [A]_t}{t} = \frac{1000 - 100}{60} = \frac{900}{60} = 15$$

$$k = \frac{1000 - 10}{120} = \frac{990}{120}$$

$$n = 1$$

$$k = \frac{2.303}{60} \log \frac{1000}{10} = \frac{2.303}{60}$$

$$k = \frac{2.303}{120} \log \frac{1000}{10} = \frac{2.303}{60}$$

(4) Ostwald Isolation method

$$\text{rate} = k[A]^m [B]^n [C]^o [D]^p \text{ - - - - -}$$

Experiment 1 : [A] = In small quantity ; [B], [C], [D] - - - - - in excess

The rate equation reduces to

$$\text{rate} = k' [A]^m \Rightarrow r_1 = k' [A]_1^m$$

$$r_2 = k' [A]_2^m$$

$$\frac{r_1}{r_2} = \left(\frac{[A]_1}{[A]_2} \right)^m, \quad \log \left(\frac{r_1}{r_2} \right) = m \log \left(\frac{[A]_1}{[A]_2} \right)$$

$$m = \frac{\log (r_1/r_2)}{\log ([A]_1/[A]_2)}$$

Experiment 2: [B] = In small quantity . & [A], [C], [D] - - - - - \Rightarrow in excess.

$$\text{rate} = k' [B]^n \rightarrow \text{repeated}$$



$$\text{Order of reaction} = m + n + o + p + \text{ - - - - -}$$

ACTIVATION ENERGY (E_a)

A mixture of magnesium and oxygen does not react at room temperature. But if a burning splinter is introduced to the mixture, it burns vigorously. Similarly a mixture of methane and oxygen does not react at room temperature, but if a burning match-stick is put in the mixture, it burns rapidly. Why it happen like this, that some external agents has to be introduced in order to initiate the reaction ?

According to the theory of reaction rates "for a chemical reaction to take place, reactant molecules must make collisions among themselves". Now in actual, only a fraction of collisions are responsible for the formation of products, i.e., not all collisions are effective enough to give products. So the collisions among reactant molecules are divided into two categories :-

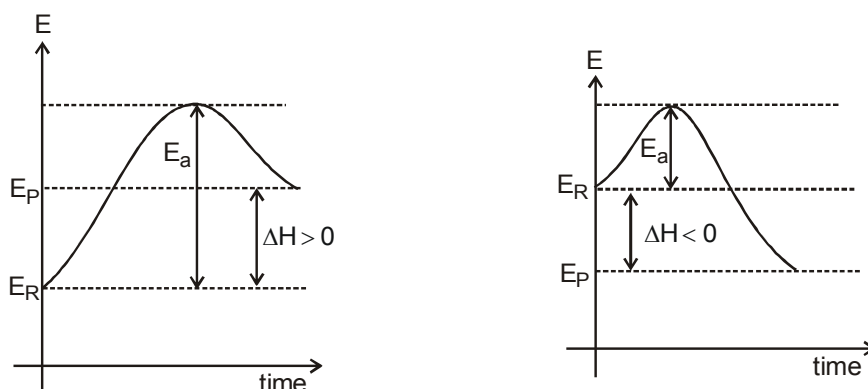
Effective collisions and In-effective collisions

Effective collisions are collisions between the molecules which have energies equal to or above a certain minimum value. This minimum energy which must be possessed by the molecules in order to make an effective collision (i.e., to give a molecule of products) is called as *threshold energy*. So it is the effective collisions which bring about the occurrence of a chemical reaction.

Ineffective collisions are the collisions between the molecules which does not posses the threshold energy. These can not result in a chemical reaction.

Now most of the times, the molecules of reactants do not possess the threshold energy. So in order to make effective collisions (i.e., to bring about the chemical reaction), an additional energy is needed to be absorbed by the reactant molecules. This additional energy which is absorbed by the molecules so that they achieve the threshold energy is called as energy of activation or simply activation energy. It is represented as E_a .

A reaction which needs higher activation energy is slow at a given temperature.

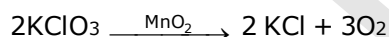


For example : $\text{NO(g)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{NO}_2\text{(g)}$ is faster at ordinary temperature whereas the following reaction :

$\text{CO(g)} + \frac{1}{2}\text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$ is slower at the same temperature as the value of E_a for the second reaction is much higher.

FACTORS AFFECTING RATE OF REACTION

- (a) **Catalyst :** The rate of reaction increased by addition of catalyst, because catalyst lowers, the activation energy and increased the rate of reaction. A catalyst is a substance which increases the rate of a reaction without itself undergoing any permanent chemical change. For example, MnO_2 catalyses the following reaction so as to increase its rate considerably.



The word catalyst should not be used when the added substance reduces the rate of reaction. The substance is then called inhibitor. The action of the catalyst can be explained by intermediate complex theory. According to this theory, a catalyst participates in a chemical reaction by forming temporary bonds with the reactants resulting in an intermediate complex. This has a transitory existence and decomposes to yield products and the catalyst.

It is believed that the catalyst provides an alternate pathway or reaction mechanism by reducing the activation energy between reactants and products and hence lowering the potential energy barrier as shown in Fig. It is clear from Arrhenius equation that lower the value of activation energy faster will be the rate of a reaction. A small amount of the catalyst can catalyse a large amount of reactants. A catalyst does not alter Gibbs energy, ΔG of a reaction. It catalyses the spontaneous reactions but does not catalyse nonspontaneous reactions. It is also found that a catalyst does not change the equilibrium constant of a reaction rather, it helps in attaining the equilibrium faster, that is, it catalyses the forward as well as the backward reactions to the same extent so that the equilibrium state remains same but is reached earlier.

- (b) **Temperature :** With increase in temperature the rate of reaction increases. It is generally found for every 10° increase in temperature. The rate constant double.

The ratio of rate constants with 10° difference in their temperature is called temperature coefficient.

$$\frac{K_{T+10}}{K_T} = Q = \text{Temperature coefficient of reaction} \approx 2$$

(c) Concentration :

$$\text{Rate} = A e^{-E_a/RT} [A]^m [B]^n \text{-----}$$

With increase in concentration of reactants the rate of the reaction increases because number of collision (effective collisions) increases.

(d) Nature of Reactants :**Ionic Reactants :**

Generally ionic reactions in aq. media are fast than the reaction involving covalent reactants. As covalent reactants involving breaking of bond then formation of bond where as ionic reaction involve in single step.

(e) Surface Area : Increase in surface area increases the number of collisions and hence rate increases**(f) Radiation :** Some reactions exposes to sunlight also increases the rate of reaction.

Collision Theory of Chemical Reactions

Though Arrhenius equation is applicable under a wide range of circumstances, collision theory, which was developed by Max Trautz and William Lewis in 1916 -18, provides a greater insight into the energetic and mechanistic aspects of reactions. It is based on kinetic theory of gases. According to this theory, the reactant molecules are assumed to be hard spheres and reaction is postulated to occur when molecules collide with each other. The number of collisions per second per unit volume of the reaction mixture is known as collision frequency (Z). Another factor which affects the rate of chemical reactions is activation energy (as we have already studied). For a bimolecular elementary reaction

$A + B \rightarrow \text{Products}$ rate of reaction can be expressed as

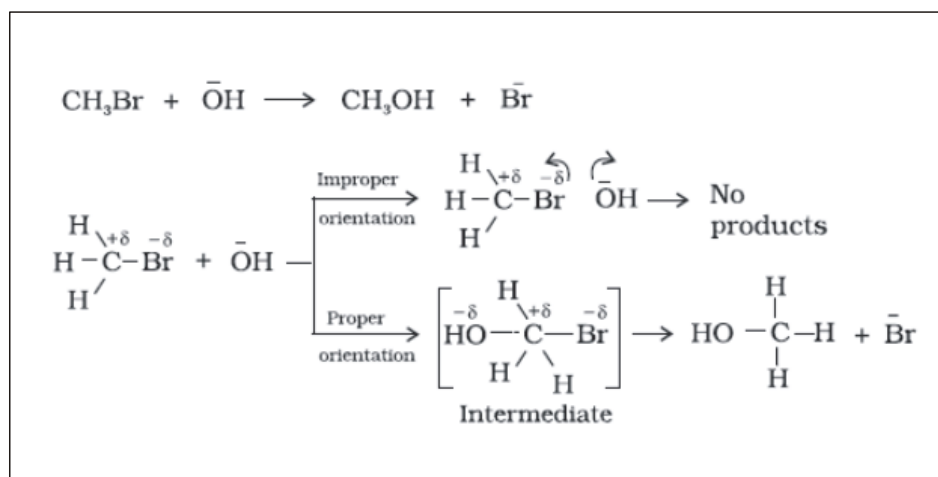
$$\text{Rate} = Z_{AB} e^{-E_a/RT} \text{.....(1)}$$

where Z_{AB} represents the collision frequency of reactants, A and B and $e^{-E_a/RT}$ represents the fraction of molecules with energies equal to or greater than E_a . Comparing (1) with Arrhenius equation, we can say that A is related to collision frequency. Equation (1) predicts the value of rate constants fairly accurately for the reactions that involve atomic species or simple molecules but for complex molecules significant deviations are observed. The reason could be that all collisions do not lead to the formation of products. The collisions in which molecules collide with sufficient kinetic energy (called threshold energy*) and proper orientation, so as to facilitate breaking of bonds between reacting species and formation of new bonds to form products are called as **effective collisions**.

To account for effective collisions, another factor P, called the probability or steric factor is introduced. It takes into account the fact that in a collision, molecules must be properly oriented i.e.,

$$\text{Rate} = PZ_{AB} e^{-E_a/RT}$$

Thus, in collision theory activation energy and proper orientation of the molecules together determine the criteria for an effective collision and hence the rate of a chemical reaction.



MECHANISM OF A REACTION

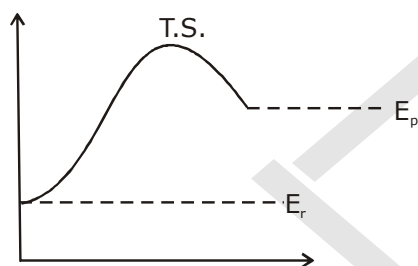
Reactions can be divided into

Elementary/Simple/single step

Complex/multi-step

ELEMENTARY REACTION :

These reaction take place in single step without formation of any intermediate



For elementary reaction we can define molecularity of the reaction which is equal to no of molecules which make transition state or activated complex because of collisions in proper orientation and with sufficient energy

molecularity will always be a natural no

1 = unimolecular one molecular gets excited (like radioactivity)

2 = bimolecular

3 = trimolecular

Molecularity ≤ 3 because the probability of simultaneous collision between 4 or more molecules in proper orientation is very low

For elementary reaction there is only single step and hence it is going to be rate determining step so order of an elementary reaction is its molecularity

Order of elementary reaction w.r.t reactant = stoichiometric co-efficient of the reactant

$\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI} \rightarrow$ Simple reaction

rate = $k [\text{H}_2] [\text{I}_2]$

$2\text{H}_2 + 2\text{I}_2 \rightleftharpoons 4\text{HI}$ (no elementary)

reaction obtained by multiplying elementary reaction with some no will not be of elementary nature

$\text{H}_2 + \text{Cl}_2 \rightleftharpoons 2\text{HCl}$

order = 0

COMPLEX REACTION :

Reaction which proceed in more than two steps or having some mechanism. (sequence of elementary reaction in which any complex reaction proceeds)

For complex reaction each step of mechanism will be having its own molecularity but molecularity of

net complex reaction will not be defined.

Order of complex reaction can be zero fractions whole no, even negative w.r.t some species.

Order of reaction or rate law of reaction is calculated with the help of mechanism of the reaction generally using rate determine step (R.D.S) if given.

Rate law of a reaction is always written in terms of conc. of reactant, products or catalysts but never in terms of conc. of intermediates.

The mechanism of any complex reaction is always written in terms of elementary steps, so molecularity of each of these steps will be defined but net molecularity of complex reaction has no meaning.

The mechanism of most of the reaction will be calculated or predicted by using mainly the following approximation.

The Rate-Determining-Step Approximation %

In the rate-determining-step approximation (also called the rate-limiting-step approximation or the equilibrium approximation), the reaction mechanism is assumed to consist of one or more reversible reactions step, which in turn is followed by one or more rapid reactions. In special cases, there may be no equilibrium steps before the rate-determining step or no rapid reactions after the rate-determining step.

As an example, consider the following mechanism composed of unimolecular (elementary) reaction.



When steps 2 $B \rightleftharpoons C$ is assumed to be the rate-determining step. For this assumption to be valid, we must have $k_{-1} \gg k_2$. The slow of $B \rightarrow C$ compared with $B \rightarrow A$ ensures that most B molecules go back to A rather than going to C, thereby ensuring that step 1 ($A \rightleftharpoons B$) remains close to equilibrium. Further-more, we must have $k_3 \gg k_2$ and $k_3 \gg k_{-2}$ to ensure that step 2 acts as a "bottleneck" and that product D is rapidly formed from C. The overall rate is then controlled by the rate-determining step $B \rightarrow C$. (Note that since $k_3 \gg k_{-2}$, the rate-limiting step is not in equilibrium.) Since we are examining the rate of the forward reaction $A \rightarrow D$, we further assume that $k_2[B] \gg k_{-2}[C]$. During the early stage of the reaction, the concentration of C will be low compared with B, and this condition will hold. Thus we neglect the reverse reaction for step 2. Since the rate-controlling step is taken to be essentially irreversible, it is irrelevant whether the rapid steps after the rate-limiting step are reversible or not. The observed rate law will, depends only on the nature of the equilibria that precede the rate-determining step and on this step itself.

ARRHENIUS EQUATION

Number of effective collisions = Number of collision \times fraction.

$$k = A e^{-E_a/RT}$$

Where,

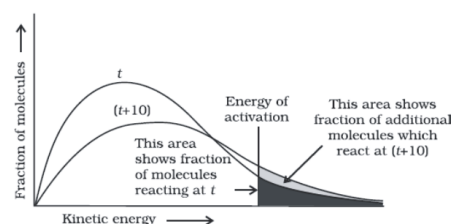
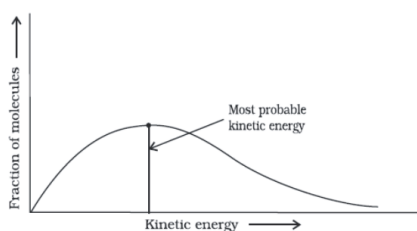
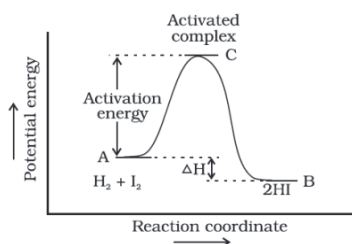
k = rate constant of reaction

A = Pre exponential factor or Arrhenius constant or Frequency factor.

E_a = Activation energy

R = Universal gas constant

T = Absolute temperature.





$$\text{Fraction of molecules undergoing effective collision} = e^{-E_a / RT} = \frac{K}{A}$$

Variation in Arrhenius equation

Type -1 :

$$\log k = 2 - \frac{5 \times 10^3}{T} ; \quad A = ? \quad E_a = ?$$

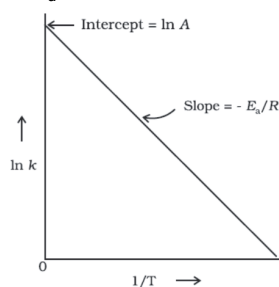
$$k = Ae^{-E_a/RT}$$

$$\log_e k = \log_e A - \frac{E_a}{RT}$$

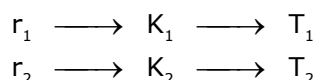
$$\log k = \log A - \frac{E_a}{2.303 RT}$$

$$\log_{10} A = 2 \Rightarrow A = 10^2 = 100$$

$$\frac{E_a}{2.303 RT} = \frac{5 \times 10^3}{T} \Rightarrow E_a = 2.303 \times R \times 5 \times 10^3$$



Type -2 : Temperature Variation :

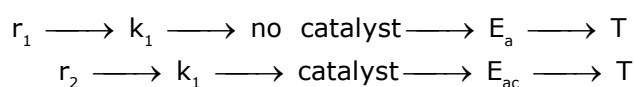
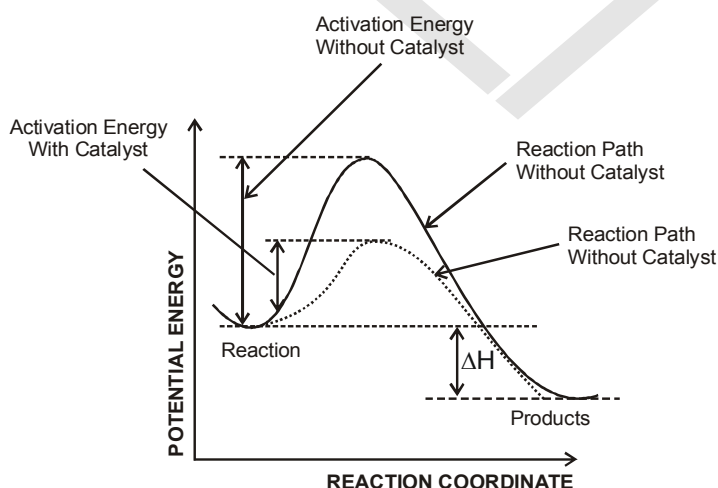


$$\frac{r_2}{r_1} = \frac{k_2}{k_1}$$

$$\log k_1 = \log A - \frac{E_a}{2.303 RT_1}, \quad \log k_2 = \log A - \frac{E_a}{2.303 RT_2}$$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

Type -3 : Addition of Catalyst :



$$\log k_1 = \log A - \frac{E_a}{2.303 RT}$$

$$\log k_2 = \log A - \frac{E_{ac}}{2.303 RT}$$

$$\log \frac{k_2}{k_1} = \frac{E_a - E_{ac}}{2.303 RT}$$

Type -4 : Both Catalyst and Temperature :

$$\log \frac{k_2}{k_1} = \frac{1}{2.303 R} \left[\frac{E_a}{T_1} - \frac{E_{ac}}{T_2} \right]$$

Problem : 8

At 278 °C the half life period for the first order thermal decomposition of ethylene oxide is 363 min and the energy of activation of the reaction is 52,00 cal/mole. From these data estimate the time required for ethylene oxide to be 75% decomposed at 450°C.

Sol. $\ln \frac{k_{450}}{k_{278}} = \frac{5200}{2} \left[\frac{1}{551} - \frac{1}{725} \right] = 1.122$

$$\frac{k_{450}}{k_{278}} = 3.07 = \frac{363}{t_{1/2}(\text{at } 450^\circ\text{C})} \quad t_{1/2}(\text{at } 450^\circ\text{C}) = 118.24 \text{ min.}$$

$$\text{Now } t_{0.75} = \frac{1}{k} \ln \frac{A_0}{A_0/4} = \frac{1}{k} \ln 4 = \frac{1.386}{k}$$

$$\therefore t_{0.75} = \frac{1.386}{0.693} \times 118.24 = \mathbf{236.48 \text{ min}}$$

Problem : 9

The activation energy of the reaction : $A + B \rightarrow \text{products}$ is 102.9 kJ/mol. At 40°C, the products are formed at the rate of 0.133 mol/L/min. What will be rate of formation of products at 80°C?

Sol. Let the rate law be defined as

$$\text{At } T_1 : r_1 = k_1 [A]^x [B]^y$$

$$\text{At } T_2 : r_2 = k_2 [A]^x [B]^y$$

$$\Rightarrow r_2 = r_1 \left(\frac{k_2}{k_1} \right)$$

Using Arrhenius equation find k at 40°C.

$$\log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left(\frac{T_2 - T_1}{T_1 T_2} \right) \Rightarrow \log_{10} \frac{k_2}{k_1} = \frac{102.9 \times 10^3}{2.303 \times 8.31} \left(\frac{40}{313 \times 353} \right)$$

$$\Rightarrow \log_{10} \frac{k_2}{k_1} = 1.95 \quad \Rightarrow \frac{k_2}{k_1} = 88.41$$

$$\Rightarrow r_2 = 0.133 \times 88.41 = 11.76 \text{ mol/L/min}$$

Problem : 10

The activation energy of a non-catalysed reaction at 37°C is 200 kcal/mol and the activation energy of the same reaction when catalysed decreases to only 6.0 kcal/mol. Calculate the ratio of rate constants of the two reactions.

Sol. We know that :

$$k = A e^{-E_a/RT}$$

Let k = rate constant for non-catalysed reaction and k_c rate constant for catalysed reaction. Let E_a be the activation energy for non-catalysed reaction and E_{ac} be the energy of activation of catalysed reaction.

$$1. \quad k = A e^{-E_a/RT}$$

$$2. \quad k_c = A e^{-E_{ac}/RT}$$

$$\Rightarrow \frac{k}{k_c} = e^{\frac{1}{RT}(E_{ac} - E_a)} \Rightarrow \log_{10} \frac{k}{k_c} = \frac{1}{2.303RT} (E_{ac} - E_a)$$

$$\Rightarrow \log_{10} \frac{k}{k_c} = \frac{1}{2.303 \times 2 \times 310} (6 \times 10^3 - 200 \times 10^3)$$

$$\Rightarrow \log_{10} \frac{k}{k_c} = -9.8 \Rightarrow \frac{k}{k_c} = 1.56 \times 10^{-10} \quad \text{or} \quad \frac{k_c}{k} = 6.3 \times 10^9$$

Problem : 11

A first order reaction $A \rightarrow B$ requires activation energy of 70 kJ/mol. When 20% solution of A was kept at 25°C for 20 minutes, 25% decomposition took place. What will be the percent decomposition in the same time in a 30% solution maintained at 40°C? Assume that the activation energy remains constant in this range of temperature.

Sol. Note : It does not matter whether you take 20%, 30%, 40% or 70% of A.

At 25°C, 20% of A decomposes 25%

$$\Rightarrow kt = 2.303 \log_{10} \frac{A_0}{A}$$

$$\Rightarrow k(40) = 2.303 \log_{10} \frac{100}{75} \Rightarrow k(\text{at } 25^\circ \text{C}) = 0.0143 \text{ min}^{-1}$$

Using Arrhenius equation find k at 40°C.

$$\log_{10} \frac{k_{40^\circ}}{k_{25^\circ}} = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\log_{10} \frac{k_{40^\circ}}{0.0143} = \frac{70 \times 10^3}{2.303 \times 8.31} \left(\frac{40 - 25}{298 \times 313} \right) \Rightarrow k(\text{at } 40^\circ \text{C}) = 0.055 \text{ min}^{-1}$$

Now calculate % decomposition at 40°C using first order kinetics.

$$kt = 2.303 \log_{10} \frac{A_0}{A}$$

$$\Rightarrow 0.055 \times 40 = 2.303 \log_{10} \frac{100}{100 - x}$$

$$\Rightarrow x = 67.1 \equiv 67.1\% \text{ decomposition of A at } 40^\circ \text{C.}$$

Problem : 12

The rate constant of a reaction is $1.5 \times 10^7 \text{ sec}^{-1}$ at 50°C and $4.5 \times 10^7 \text{ sec}^{-1}$ at 100°C . Evaluate the Arrhenius parameters A and E_a .

$$\text{Sol.} \quad \therefore 2.303 \log_{10} \frac{K_2}{K_1} = \frac{E_a}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\therefore 2.303 \log_{10} \frac{4.5 \times 10^7}{1.5 \times 10^7} = \frac{E_a}{8.314} \left[\frac{373 - 323}{373 \times 323} \right]$$

$$\therefore E_a = 2.2 \times 10^4 \text{ J mol}^{-1}$$

$$\text{Now,} \quad K = Ae^{-E_a/RT} \quad \therefore 4.5 \times 10^7 = Ae^{-\frac{2.2 \times 10^4}{8.314 \times 373}}$$

$$\therefore A = 5.42 \times 10^{10}$$

Problem : 13

A reaction proceeds five times more at 60°C as it does at 30°C . Estimate energy of activation.

$$\text{Sol.} \quad \text{Given, } T_2 = 60 + 273 = 333 \text{ K, } T_1 = 30 + 273 = 303 \text{ K,}$$

$$R = 1.987 \times 10^{-3} \text{ kcal}$$

$$\therefore r = k []^n \quad (\text{at a temperature } T)$$

$$\therefore \frac{r_2}{r_1} = \frac{K_2}{K_1} \quad (\text{at temp. } T_2 \text{ and } T_1)$$

$$\therefore \frac{r_2}{r_1} = 5 \quad \therefore \frac{K_2}{K_1} = 5$$

$$\therefore 2.303 \log_{10} \frac{K_2}{K_1} = \frac{E_a}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\therefore 2.303 \log_{10} 5 = \frac{E_a}{10^{-3} \times 1.987} \left[\frac{333 - 303}{333 \times 303} \right]$$

$$E_a = 10.757 \text{ kcal mol}^{-1}$$

Problem : 14

The rate constant of a reaction increases by 7% when its temperature is raised from 300 K to 310 K, while its equilibrium constant increases by 3%. Calculate the activation energy of the forward and reverse reactions.

$$\text{Sol.} \quad \text{Rate constant at } 300\text{K} = k$$

$$\therefore \text{Rate constant at } 310 \text{ K} = k + \left[k \times \frac{7}{100} \right] = 1.07 k$$

$$\text{Thus,} \quad 2.303 \log \frac{k_2}{k_1} = \frac{E_a^f}{R} \left[\frac{T_2 - T_1}{T_2 T_1} \right]$$

$$2.303 \log \frac{1.07k}{k} = \frac{E_a^f}{2} \left[\frac{310 - 300}{310 \times 300} \right]$$

$$\therefore E_a^f = 1258.68 \text{ cal}$$

Now, equilibrium constant at 300 K = K'

$$\text{Equilibrium constant at 310 K} = K' + \frac{3}{100} \times K' = 1.03 K'$$

$$\text{Using } 2.303 \log \frac{K_2}{K_1} = \frac{\Delta H}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$2.303 \log \frac{1.03 K'}{K'} = \frac{\Delta H}{2} \left[\frac{310 - 300}{310 \times 300} \right]$$

$$\therefore \Delta H = 549.89 \text{ cal}$$

$$\text{Since, } \Delta H = E_a^f - E_a^b$$

$$\therefore 549.89 = 1258.68 - E_a^b$$

$$\therefore E_a^b = 708.79 \text{ cal}$$

Problem : 15

At 380°C, the half life period for the first order decomposition of H_2O_2 is 360 min. The energy of activation of the reaction is 200 kJ mol^{-1} . Calculate the time required for 75% decomposition at 450°C.

[IIT 1995]

Sol. $K_1 = 0.693/360 \text{ min}^{-1}$ at 653 K and

$$E_a = 200 \times 10^3 \text{ J}, \quad K_2 = ? \text{ at } 723 \text{ K}, \quad R = 8.314 \text{ J}$$

$$\therefore \text{From } 2.303 \log_{10} (K_2 / K_1) = (E_a/R)[(T_2 - T_1)/(T_1 T_2)]$$

$$K_2 = 0.068 \text{ min}^{-1}$$

$$\text{Now, } t = \frac{2.303}{0.068} \log_{10} \frac{100}{25} = 20.39 \text{ minute}$$

OBJECTIVE SOLVED PROBLEMS

Problem : 1

In gaseous reactions important for understanding of the upper atmosphere H_2O and O react bimolecularly to form two OH radicals. ΔH for this reaction is 72 kJ/mol at 500 K and $E_a = 77 \text{ kJ/mol}$, then E_a for two bimolecular recombination of 2OH radicals to form H_2O & O is

(A) 3 kJ mol^{-1} (B) 4 kJ mol^{-1}

(C) 5 kJ mol^{-1} (D) 7 kJ mol^{-1}

Sol. As ΔH is positive, therefore reaction is endothermic

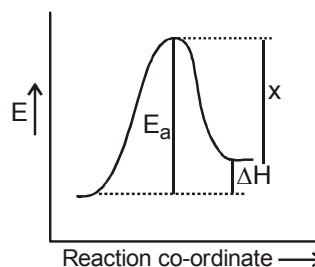
This is the energy profile diagram for an endothermic reaction.

Now when the products is converted back to reactant the energy of activation is x as shown in fig.

$$\text{Evidently } x = E_a - \Delta H$$

$$= (77 - 72) = 5 \text{ kJ mol}^{-1}$$

$$\therefore \text{(C)}$$



Problem : 2

In a certain reaction 10% of the reactant decomposes in the first hour, 20% in second hour, 30% in third hour and so on. What are the dimensions of rate constant.

- (A) hour^{-1} (B) $\text{mol lit}^{-1} \text{sec}^{-1}$ (C) $\text{lit mol}^{-1} \text{sec}^{-1}$ (D) mol sec^{-1}

Sol. If the amount of products formed which is 10%, 20% and 30% is plotted against time i.e., 1 hr, 2 hr and 3 hr respectively, it is a straight line passing through the origin.

$$\therefore \text{it is a zero order reaction where } x = kt \Rightarrow \frac{x}{t} = k$$

$$\therefore \text{dimensions of } k = \text{moles lit}^{-1} \text{sec}^{-1}$$

\therefore (B)

Problem : 3

Two substances A ($t_{1/2} = 5 \text{ mins}$) and B ($t_{1/2} = 15 \text{ mins}$) are taken in such a way that initially $[A] = 4[B]$. The time after which the concentration of both will be equal is

- (A) 5 min (B) 15 min
(C) 20 min (D) concentration can never be equal

Sol. $t_{1/2}$ of A is 5 min

\therefore in 15 mins it will become $1/8$ of initial and $t_{1/2}$ of B is 15 mins

\therefore in 15 mins it will become $1/2$ of initial

\therefore ratio of $[A] : [B]$ after 15 min is 4 : 1

But given $[A] = 4[B]$

$\therefore [A] = [B]$ after 15 min

\therefore [B]

Problem : 4

The reaction $A(g) + 2B(g) \rightarrow C(g) + D(g)$ is an elementary process. In an experiment, the initial partial pressure of A & B are $P_A = 0.60$ and $P_B = 0.80 \text{ atm}$. When $P_C = 0.2 \text{ atm}$ the rate of reaction relative to the initial rate is

- (A) $1/48$ (B) $1/24$ (C) $9/16$ (D) $1/6$

Sol.

	A(g)	+	2B(g)	\rightarrow	C(g)	+	D(g)
t = 0	0.60		0.80		0		0
t = t	(0.6 - 0.2)		(0.8 - 2 \times 0.2)		0.2		0.2

$$(\text{Rate})_i = k[A][B]^2 = k[0.6][0.8]^2$$

$$(\text{Rate})_t = k[0.4][0.4]^2$$

$$\frac{R_t}{R_i} = \frac{k[0.4]^3}{k[0.6][0.8]^2} = \frac{1}{6} \quad \therefore \text{[D]}$$

Problem : 5

For a hypothetical reaction $A + B \rightarrow C + D$, the rate $= k[A]^{-1/2}[B]^{3/2}$. On doubling the concentration of A and B the rate will be

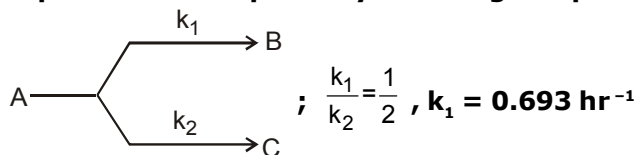
- (A) 4 times (B) 2 times (C) 3 times (D) none of these

Sol. $k = k[2]^{-1/2}[2]^{3/2} = k[2]^{3/2-1/2} = k = [2]^1 = 2k$

\therefore [B]

Problem : 6

An organic compound A decomposes by following two parallel first order mechanisms :



Select the correct statement(s)

- (A) If three moles of A are completely decomposed then 2 moles of B and 1 mole of C will be formed.
 (B) If three moles of A are completely decomposed then 1 moles of B and 2 mole of C will be formed.
 (C) half life for the decomposition of A is 20 min
 (D) half life for the decomposition of B is 0.33 min

Sol. BC

$$k = k_1 + k_2 = 0.693 + 2 \times 0.693$$

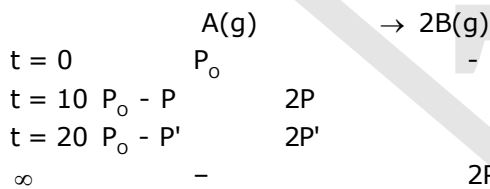
$$\frac{0.693}{t_{1/2}} = 3 \times 0.693 \Rightarrow t_{1/2} = \frac{1}{3} \text{ hr} = 20 \text{ min}$$

Problem : 7

For any 1st order gaseous reaction $\text{A} \rightarrow 2\text{B}$ Pressure developed after 20 min is 16.4 atm and after very long time is 20 atm. What is the total pressure developed after 10 min.

- (A) 12 (B) 13 (C) 14 (D) 15

Sol. C



$$2P_0 = 20 \Rightarrow P_0 = 10$$

$$16.4 = P_0 - P' + 2P'$$

$$16.4 = 10 + P'$$

$$P' = 6.4$$

for first order reaction at equal time conc/pr is in G. P.

$$\frac{P_0 - P'}{P_0 - P} = \frac{P_0 - P}{P_0} \quad , \quad \frac{10 - 6.4}{10 - P} = \frac{10 - P}{10}$$

$$3.6 \times 10 = (10 - P)^2$$

\Downarrow

$$10 - P = 6$$

$$P = 4$$

$$P_{10 \text{ min}} = P_0 + P = 10 + 4 = 14 \text{ atm}$$

Problem : 8

For any reaction, $2A \rightarrow B$, rate constant of reaction is 0.231 min^{-1} . Time (in sec) when 25% of A will remain unreacted.

- (A) 150 (B) 180 (C) 200 (D) 140

Sol. B

$$k_r = \frac{k_A}{2}, \quad t_{75\%} = 2t_{1/2} = \frac{0.693}{2k_r} \times 2$$

$$= 3 \text{ min}$$

$$= 180 \text{ sec}$$

Problem : 9

For any reaction $A(g) \rightarrow B(g)$, rate constant $k = 8.21 \times 10^{-2} \text{ atm/min}$ at 300 K. If initial concentration of A is 2M then what is the half life (in hr.)?

- (A) 5 (B) 6 (C) 7 (D) 8

Sol. A

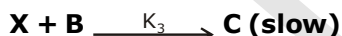
$$\text{Rate} = k = \frac{8.21 \times 10^{-2} \text{ atm}}{0.0821 \times 300 \text{ min}} = \frac{1}{300} \frac{\text{mole}}{\ell \cdot \text{min}}$$

$$t_{1/2} = \frac{a}{2k} = \frac{2}{2k} = \frac{1}{k} = 300 \text{ min}$$

$$= 5 \text{ hr.}$$

Problem : 10

The mechanism of the above reaction given as



E_1 = Activation energy for K_1

E_2 = Activation energy for K_2

E_3 = Activation energy for K_3

Calculate E_{reaction}

(given : $E_1 = 10 \text{ kJ}$, $E_3 = 5 \text{ kJ}$, $E_2 = 12 \text{ kJ}$)

- (A) 5 (B) 6 (C) 7 (D) 3

Sol. D

$$\text{rate} = K_3 [X][B]$$

$$\frac{k_1}{k_2} = \frac{[X][B]^2}{[A]^2}, [X] = \frac{k_1}{k_2} \frac{[A]^2}{[B]^2}$$

$$\text{rate} = k_3 \cdot \frac{k_1}{k_2} \cdot \frac{[A]^2[B]}{[B]^2}, = k_3 \cdot \frac{k_1}{k_2} \cdot \frac{[A]^2}{[B]}$$

$$K_{\text{eff}} = \frac{k_3 \cdot k_1}{k_2}, E_{\text{total}} = E_1 + E_3 - E_2$$

$$= 3 \text{ kJ}$$

SUBJECTIVE SOLVED PROBLEMS**Problem : 1**

The rate of change of concentration of C in the reaction $2A + B \rightarrow 2C + 3D$ was reported as $1.0 \text{ mol litre}^{-1} \text{ sec}^{-1}$. Calculate the reaction rate as well as rate of change of concentration of A, B and D.

Sol. We have,

$$-\frac{1}{2} \frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{1}{2} \frac{d[C]}{dt} = \frac{1}{3} \frac{d[D]}{dt} = \text{rate of reaction}$$

$$\therefore \frac{d[C]}{dt} = 1.0 \text{ mol litre}^{-1} \text{ sec}^{-1}$$

$$\therefore -\frac{d[A]}{dt} = \frac{d[C]}{dt} = \mathbf{1.0 \text{ mol L}^{-1} \text{ sec}^{-1}}$$

$$-\frac{d[B]}{dt} = \frac{1}{2} \frac{d[C]}{dt} = \frac{1}{2} = \mathbf{0.5 \text{ mol L}^{-1} \text{ sec}^{-1}}$$

$$\frac{d[D]}{dt} = \frac{3}{2} \frac{d[C]}{dt} = \frac{3}{2} \times 1 = \mathbf{1.5 \text{ mol L}^{-1} \text{ sec}^{-1}}$$

Also,

$$\therefore \text{Rate} = \frac{1}{2} \frac{d[C]}{dt}$$

$$\therefore \text{Rate} = \frac{1}{2} \times 1 = \mathbf{0.5 \text{ mol L}^{-1} \text{ sec}^{-1}}$$

Problem : 2

For the reaction $A + B \rightarrow C$, the following data were obtained. In the first experiment, when the initial concentrations of both A and B are 0.1 M , the observed initial rate of formation of C is $1 \times 10^{-4} \text{ mol litre}^{-1} \text{ minute}^{-1}$. In the second experiment when the initial concentrations of A and B are 0.1 M and 0.3 M , the initial rate is $9.0 \times 10^{-4} \text{ mol litre}^{-1} \text{ minute}^{-1}$.

(a) Write rate law for this reaction

(b) Calculate the value of specific rate constant for this reaction.

Sol. Let $\text{Rate} = K[A]^m[B]^n$

$$(a) \quad r_1 = 1 \times 10^{-4} = K[0.1]^m [0.1]^n \quad \dots(1)$$

$$r_2 = 9 \times 10^{-4} = K[0.1]^m [0.3]^n \quad \dots(2)$$

$$r_3 = 2.7 \times 10^{-3} = K[0.3]^m [0.3]^n \quad \dots(3)$$

By Eqs. (1) and (2),

$$\frac{r_1}{r_2} = \frac{1 \times 10^{-4}}{9 \times 10^{-4}} = \left(\frac{1}{3}\right)^n$$

$$\therefore n = 2$$

By Eqs. (2) and (3),

$$\frac{r_2}{r_3} = \frac{9 \times 10^{-4}}{27 \times 10^{-4}} = \left(\frac{1}{3}\right)^m \quad m = 1$$

$$\therefore \text{Rate} = \mathbf{K[A]^1[B]^2}$$

$$(b) \quad \text{Also by Eq. (1),} \quad 1 \times 10^{-4} = K[0.1]^1 [0.1]^2$$

$$K = \mathbf{10^{-1} = 0.1 \text{ L}^2 \text{ mol}^{-2} \text{ min}^{-1}}$$

Problem : 3

The chemical reaction between $K_2C_2O_4$ and $HgCl_2$ is ;



The weights of Hg_2Cl_2 precipitated from different solutions in given time were taken and expressed as following :

Time (minutes)	$HgCl_2$ (M)	$K_2C_2O_4$ (M)	Hg_2Cl_2 formed (M)
60	0.0418	0.404	0.0032
65	0.0836	0.404	0.0068
120	0.0836	0.202	0.0031

Let the rate law be written as : $r = k[HgCl_2]^x [K_2C_2O_4]^y$

$$1. \quad \frac{0.0032}{60} = k[0.0418]^x [0.404]^y$$

$$2. \quad \frac{0.0068}{65} = k[0.0836]^x [0.404]^y$$

$$3. \quad \frac{0.0031}{120} = k[0.0836]^x [0.202]^y$$

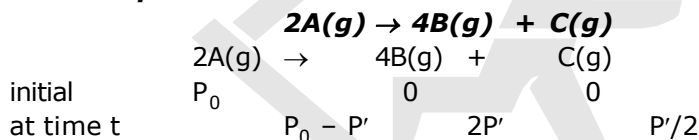
Solving the above equations, we get :

$x = 1$ and $y = 2 \quad \Rightarrow \quad$ order of reaction w.r.t $x = 1$ and $y = 2$ and overall order is 3.

Problem : 4

The reaction given below, involving the gases is observed to be first order with rate constant $7.48 \times 10^{-3} \text{ sec}^{-1}$. Calculate the time required for the total pressure in a system containing A at an initial pressure of 0.1 atm to rise to 0.145 atm also find the total pressure after 100 sec.

Sol.



$$P_{\text{total}} = P_0 - P' + 2P' + P'/2 = P_0 + \frac{3P'}{2}$$

$$P' = \frac{2}{3}(0.145 - 0.1) = 0.03 \text{ atm}$$

$$k = \frac{2.303}{2t} \log \frac{P_0}{P_0 - P'}$$

$$t = \frac{2.303}{7.48 \times 10^{-3} \times 2} \log \left(\frac{0.1}{0.07} \right)$$

$$t = 23.84 \text{ sec}$$

$$\text{Also, } k = \frac{2.303}{2t} \log \left(\frac{0.1}{P_0 - P'} \right)$$

$$7.48 \times 10^{-3} = \frac{2.303}{2 \times 100} \log \left(\frac{0.1}{0.1 - P'} \right)$$

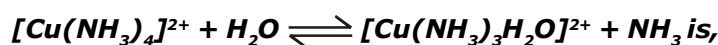
$$0.1/0.1 - P' = 5$$

$$P' = 0.08$$

$$P_{\text{total}} = 0.1 + \frac{3}{2}(0.080) \quad \approx \quad 0.22 \text{ atm.}$$

Problem : 5

The net rate of reaction of the change :



$$\frac{dx}{dt} = 2.0 \times 10^{-4} [\text{Cu}(\text{NH}_3)_4]^{2+} - 3.0 \times 10^5 [\text{Cu}(\text{NH}_3)_3\text{H}_2\text{O}]^{2+} [\text{NH}_3]$$

calculate :

(i) rate expression for forward and backward reactions.

(ii) the ratio of rate constant for forward and backward reactions.

(iii) the direction of reaction in which the above reaction will be more predominant.

Sol. (i) Rate of forward reaction = $2.0 \times 10^{-4} [\text{Cu}(\text{NH}_3)_4]^{2+} [\text{H}_2\text{O}]$
 Rate of backward reaction = $3.0 \times 10^5 [\text{Cu}(\text{NH}_3)_3\text{H}_2\text{O}]^{2+} [\text{NH}_3]$

(ii) Also, $K_f = 2.0 \times 10^{-4}$
 $K_b = 3.0 \times 10^5$

$$\therefore \frac{K_f}{K_b} = \frac{2.0 \times 10^{-4}}{3.0 \times 10^5} = 6.6 \times 10^{-10}$$

(iii) More predominant reaction is **backward reaction**.

Problem : 6

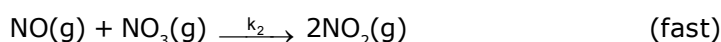
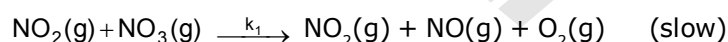
The rate law for the decomposition of gaseous N_2O_5



is observed to be

$$r = -\frac{d[\text{N}_2\text{O}_5]}{dt} = k[\text{N}_2\text{O}_5]$$

A reaction mechanism which has been suggested to be consistent with this rate law is



Show that the mechanism is consistent with the observed rate law.

Since the slow step is the rate determining step, hence

$$r = k_1[\text{NO}_2][\text{NO}_3] \quad \dots(1)$$

and from the fast equilibrium step,

$$K = \frac{[\text{NO}_2][\text{NO}_3]}{[\text{N}_2\text{O}_5]}$$

$$\text{Thus, } [\text{NO}_2][\text{NO}_3] = K[\text{N}_2\text{O}_5] \quad \dots(ii)$$

Using (ii) in (i), we get :

$$r = k_1 K [\text{N}_2\text{O}_5] = k [\text{N}_2\text{O}_5] \quad \text{where } k = k_1 K$$

This shows that the mechanism is consistent with the observed rate law.

Problem : 7

The half life of first order decomposition of nitramide is 2.1 hour at 15°C.



If 6.2 gm of NH_2NO_2 is allowed to decompose, find :

- (a) time taken for nitramide to decompose 99%;
 (b) volume of dry N_2O gas produced at this point at STP.

Sol. (a) Using first order kinetics, we have :

$$kt = 2.303 \log_{10} \frac{A_0}{A}$$

$$\Rightarrow \frac{0.693}{2.1} \times t = 2.303 \log_{10} \frac{100}{100-99} \Rightarrow t = 13.96 \text{ hours}$$

- (b) 6.2 gm of $\text{NH}_2\text{NO}_2 \equiv 0.1 \text{ mol}$
 and 1 mole $\text{NH}_2\text{NO}_2 \equiv 1 \text{ mole of } \text{N}_2\text{O}$
 As 99% of NH_2NO_2 is decomposed
 $\Rightarrow 0.099 \text{ mol of } \text{NH}_2\text{NO}_2$ is decomposed
 0.099 mol of N_2O are produced $\equiv 22.4 \times 0.099 = 2.217 \text{ L of } \text{N}_2\text{O}$ at STP.

Problem : 8

The reaction $\text{A} + \text{OH}^- \rightarrow \text{Products}$, obeys rate law expression as,

$$\frac{-d[\text{A}]}{dt} = k[\text{A}][\text{OH}^-]$$

If initial concentrations of $[\text{A}]$ and $[\text{OH}^-]$ are 0.002 M and 0.3 M respectively and if it takes 30 sec for 1% A to react at 25°C, calculate the rate constant for the reactions.

Sol.

	A	+	OH ⁻	→	Products
--	---	---	-----------------	---	----------

t = 0	0.002		0.3		
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t = 30	$\left[0.002 - \frac{0.002 \times 1}{100}\right]$		$\left[0.3 - \frac{0.002 \times 1}{100}\right]$		
--------	---	--	---	--	--

$$\text{Using } K = \frac{2.303}{t(a-b)} \log_{10} \frac{b(a-x)}{a(b-x)}$$

$$K = \frac{2.303}{30 \times (0.002 - 0.3)} \log_{10} \frac{0.3 \times \left[0.002 - \frac{0.002 \times 1}{100}\right]}{0.002 \left[0.3 - \frac{0.002 \times 1}{100}\right]}$$

$$K = 1.12 \times 10^{-3} \text{ L mol}^{-1} \text{ sec}^{-1}$$

Problem : 9

A certain reaction $\text{A} + \text{B} \rightarrow \text{products}$; is first order w.r.t. each reactant with $k = 5.0 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$. Calculate the concentration of A remaining after 100s if the initial concentration of A was 0.1 M and that of B was 6.0 M. State any approximation made in obtaining your result.

Sol. $A + B \rightarrow \text{products}$

Given : Rate = $k[A][B]$ (2nd Order reaction)

Now, since $[B] \gg [A]$, $[B]$ can be assumed to remain constant throughout the reaction. Thus, the rate law for the reaction, becomes :

$$\text{Rate} \approx k_0[A] \quad \text{where } k_0 = k[B] = 5.0 \times 10^{-3} \times 6.0 \text{ s}^{-1} = 3.0 \times 10^{-2} \text{ s}^{-1}$$

Thus, the reaction is now of first order.

$$\text{Using, } 2.303 \log_{10} \frac{A_0}{A} = k_0 t$$

$$\Rightarrow 2.303 \log_{10} \frac{0.1}{A} = k_0 t = 3$$

$$\Rightarrow \log_e \frac{0.1}{A} = 3 \quad [\because \log_e x = 2.303 \log_{10} x]$$

$$\Rightarrow A = \frac{0.1}{e^3} = 5 \times 10^{-3} \text{ M}$$

Problem : 10

Dimethyl ether decomposes according to the following reaction :



At a certain temperature, when ether was heated in a closed vessel, the increase in pressure with time was noted down.

Time (min)	0	10	20	30
Pressure (mm Hg)	420	522	602	678

(i) Show that the reaction is first order.

(ii) Compute the pressure of CO(g) after 25 minutes.

Sol. $\text{CH}_3 - \text{O} - \text{CH}_3(\text{g}) \rightarrow \text{CH}_4(\text{g}) + \text{CO}(\text{g}) + \text{H}_2(\text{g})$ (all are gases)

time	$\text{CH}_3\text{-O-CH}_3$	CH_4	CO	H_2
$t = 0$	$C_0 = P_0$	0	0	0
$t = t$	$C_t = P_0 - x$	x	x	x

$$\Rightarrow P_t = P_0 + 2x$$

$$\Rightarrow x = \frac{1}{2}(P_t - P_0)$$

$$\Rightarrow \frac{A_0}{A} = \frac{P_0}{P_0 - x} = \frac{2P_0}{3P_0 - P_t}$$

Now find k_1 , k_2 and k_3 using the first order kinetics

$$k t = 2.303 \log_{10} \frac{2P_0}{3P_0 - 2P_t}$$

$$k_1 = \frac{2.303}{10} \log_{10} \frac{2(420)}{3(420) - 522} = 0.0129 \text{ min}^{-1}$$

$$k_2 = \frac{2.303}{20} \log_{10} \frac{2(420)}{3(420) - 602} = 0.0122 \text{ min}^{-1}$$

$$k_3 = \frac{2.303}{30} \log_{10} \frac{2(420)}{3(420) - 678} = 0.0123 \text{ min}^{-1}$$

As $k_1 \sim k_2 \sim k_3$, the reaction is first order.

$$k_{\text{average}} = \frac{1}{3}(k_1 + k_2 + k_3) = 0.0127 \text{ min}^{-1}$$

$$P_{\text{CO}} = x = \frac{1}{2}(P_t - P_0)$$

Find P after $t = 25$ min using first order kinetics with $k = 0.0127 \text{ min}^{-1}$

$$\Rightarrow \log_{10} \frac{2(420)}{3(240) - P_t} = 0.0127 \times 25$$

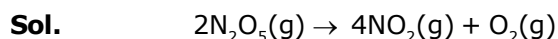
$$\Rightarrow P_t = 648.46 \text{ mm} \Rightarrow x = 114.23 \text{ mm}$$

Problem : 11

The decomposition of N_2O_5 according to following reaction is first order reaction :



After 30 min. from start of the decomposition in a closed vessel, the total pressure developed is found to be 284.5 mm of Hg and on complete decomposition, the total pressure is 584.5 mm of Hg. Calculate the rate constant of the reaction.



$2\text{N}_2\text{O}_5$	4NO_2	O_2
P_0	0	0
$P_0 - 2x$	$4x$	x

P_0 : initial pressure ; Let P_t : pressure at 30 min and P_∞ : pressure at the end of decomposition.

$$\Rightarrow P_t = P_0 + 3x \quad \Rightarrow \quad x = \frac{1}{3}(P_t - P_0)$$

$$\text{and } P_\infty = 2P_0 + \frac{1}{2}P_0 = \frac{5}{2}P_0 \quad \Rightarrow \quad P_0 = \frac{2}{5}P_\infty$$

For the first order kinetics

$$k_{\text{eff}} t = 2.303 \log_{10} \frac{A_0}{A}$$

A_0 : initial concentration ; A : final concentration

$$\text{Now } \frac{A_0}{A} = \frac{P_0}{P_0 - 2x} = \frac{\frac{1}{5}P_\infty}{\frac{1}{5}P_\infty - 2\frac{P_t - 2/5P_\infty}{3}} \Rightarrow \frac{A_0}{A} = \frac{3}{5} \left(\frac{P_\infty}{P_\infty - P_t} \right)$$

$$\Rightarrow k_{\text{eff}} = \frac{1}{30} \times 2.303 \log_{10} \frac{3}{5} \times \frac{584.5}{584.5 - 284.5} = 5.204 \times 10^{-3} \text{ min}^{-1}$$

$$k \text{ for the reaction} = \frac{5.204}{2} \times 10^{-3} = 2.602 \times 10^{-3} \text{ min}^{-1}$$

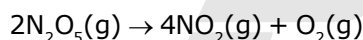
Problem : 12

The gas phase decomposition of N_2O_5 to NO_2 and O_2 is monitored by measurement of total pressure. The following data are obtained.

P_{total} (atm)	0.154	0.215	0.260	0.315	0.346
Time (sec)	1	52	103	205	309

Find the average rate of disappearance of N_2O_5 for the time interval between each interval and for the total time interval. [Hint : Integrated rate law is NOT to be used]

Sol.



Initial Pressure (at $t = 0$) P_0 0 0

At equilibrium $P_0 - 2x$ $4x$ x

$$\text{Now: } P_t = (P_0 - 2x) + 4x + x \Rightarrow x = \frac{1}{3}(P_t - P_0)$$

$$P_{\text{N}_2\text{O}_5} = P_0 - 2x = \frac{1}{3}(5P_0 - 2P_t)$$

Thus, $\Delta P_{\text{N}_2\text{O}_5} = \frac{2}{3}(P_{t_1} - P_{t_2})$ where P_{t_2} and P_{t_1} are the total pressures at time instants t_2 and t_1 ($t_2 > t_1$) respectively

P_{total} (atm)	Time (sec)	$\frac{\Delta P_{\text{N}_2\text{O}_5}}{\Delta t} = \text{Avg. Rate of disappearance of } \text{N}_2\text{O}_5$
0.154	1	$\frac{(0.154 - 0.215)}{(52 - 1)} = -1.20 \times 10^{-3}$ $\frac{(0.215 - 0.260)}{(103 - 52)} = -0.88 \times 10^{-3}$ $\frac{(0.260 - 0.315)}{(205 - 103)} = -0.54 \times 10^{-3}$ $\frac{(0.315 - 0.346)}{(309 - 205)} = -0.30 \times 10^{-3}$
0.215	52	
0.260	103	
0.315	205	
0.346	309	

Problem : 13

5 ml of ethylacetate was added to a flask containing 100 ml of 0.1 N HCl placed in a thermostat maintained at 30°C. 5 ml of the reaction mixture was withdrawn at different intervals of time and after chilling, titrated against a standard alkali. The following data were obtained :

Time (minutes)	0	75	119	183	∞
Volume of alkali used in ml	9.62	12.10	1.10	14.75	21.05

Show that hydrolysis of ethyl acetate is a first order reaction.

Sol. The hydrolysis of ethyl acetate will be a first order reaction if the above data confirm to the equation.

$$k_1 = \frac{2.303}{t} \log \frac{V_\infty - V_0}{V_\infty - V_t}$$

Where V_0 , V_t and V_∞ represent the volumes of alkali used at the commencement of the reaction, after time t and at the end of the reaction respectively, Hence

$$V_\infty - V_0 = 21.05 - 9.62 = 11.43$$

Time	$V_\infty - V_t$	k_1
75 min	$21.05 - 12.10 = 8.95$	$\frac{2.303}{75} \log \frac{11.43}{8.95} = 0.003259 \text{ min}^{-1}$
119 min	$21.05 - 13.10 = 7.95$	$\frac{2.303}{119} \log \frac{11.43}{7.95} = 0.003051 \text{ min}^{-1}$
183 min	$21.05 - 14.75 = 6.30$	$\frac{2.303}{183} \log \frac{11.43}{6.30} = 0.003254 \text{ min}^{-1}$

A constant value of k shows that hydrolysis of ethyl acetate is a **first order** reaction.

Problem : 14

The optical rotations of sucrose in 0.5N HCl at 35°C at various time intervals are given below. Show that the reaction is of first order :

Time (minutes)	0	10	20	30	40	∞
Rotation (degrees)	+32.4	+28.8	+25.5	+22.4	+19.6	-11.1

Sol. The inversion of sucrose will be first order reaction if the above data confirm to the equation, $k_1 =$

$$\frac{2.303}{t} \log \frac{r_0 - r_\infty}{r_t - r_\infty}$$

Where r_0 , r_t and r_∞ represent optical rotations initially, at the commencement of the reaction after time t and at the completion of the reaction respectively

$$\text{In the case } a_0 = r_0 - r_\infty = +32.4 - (-11.1) = +43.5$$

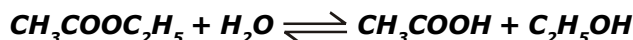
The value of k at different times is calculated as follows :

Time	r_t	$r_t - r_\infty$	k
10 min	+28.8	39.9	$\frac{2.303}{10} \log \frac{43.5}{39.9} = 0.008625 \text{ min}^{-1}$
20 min	+25.5	36.6	$\frac{2.303}{10} \log \frac{43.5}{36.6} = 0.008625 \text{ min}^{-1}$
30 min	+22.4	33.5	$\frac{2.303}{30} \log \frac{43.5}{33.5} = 0.008694 \text{ min}^{-1}$
40 min	+19.6	30.7	$\frac{2.303}{40} \log \frac{43.5}{30.7} = 0.008717 \text{ min}^{-1}$

The constancy of k_1 indicates that the inversion of sucrose is a **first order** reaction.

Problem : 15

The hydrolysis of ethyl acetate



in aqueous solution is first order with respect to ethyl acetate. Upon varying the pH of the solution the first order rate constant varies as follows.

pH	3	2	1
$k_1 \times 10^{-4} \text{ s}^{-1}$	1.1	11	110

what is the order of the reaction with respect to H^+ and the value of the rate constant?

Sol.

$$\text{Rate} = k[\text{CH}_3\text{COOC}_2\text{H}_5]^a[\text{H}^+]^b$$

$[\text{H}^+]$ is constant through out the reaction

$$k_1 = k[\text{H}^+]^b$$

$$\text{Hence, } \left(\frac{k_1}{k_1'} \right) = \left(\frac{[\text{H}^+]_1}{[\text{H}^+]_2} \right)^b \quad \frac{1.1}{11} = \left(\frac{10^{-3}}{10^{-2}} \right)^b$$

$$b = 1$$

$$k_1 = k[\text{H}^+]$$

$$1.1 \times 10^{-4} = k(10^{-3}) \Rightarrow k = 1.1 \times 10^{-1} \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$$

Problem : 16

Two I order reactions having same reactant concentrations proceed at 25°C at the same rate. The temperature coefficient of the rate of the first reaction is 2 and that of second reaction is 3. Find the ratio of the rates of these reactions at 75°C

Sol.

For I order reaction $r_1 = K_1[\text{C}]^1$

$$\therefore \frac{R_1}{R_2} = K_1 / K_2 = \text{temperature coefficient}$$

Let temperature co-efficient be a

$$\frac{R_{35}}{R_{25}} = \frac{K_{35}}{K_{25}} = a$$

$$\frac{R_{45}}{R_{35}} = \frac{K_{45}}{K_{35}} = a$$

$$\therefore \frac{R_{45}}{R_{25}} = a \times a = a^2$$

$$\text{Similarly, } \frac{R_{75}}{R_{25}} = a^5$$

$$\text{For I reaction } (R_{75})_{\text{I}} = 2^5 \times (R_{25})_{\text{I}}$$

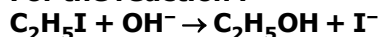
$$\text{For II reaction } (R_{75})_{\text{II}} = 3^5 \times (R_{25})_{\text{II}}$$

$$\therefore \frac{(R_{75})_{\text{II}}}{(R_{75})_{\text{I}}} = \frac{3^5}{2^5} = 7.9537$$

$$[\therefore (R_{25})_{\text{I}} = (R_{25})_{\text{II}}]$$

Problem : 17

For the reaction :



the rate constant was found to have a value of $5.03 \times 10^{-2} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ at 289 K and $6.71 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ at 333 K. What is the rate constant at 305 K.

Sol. $k_2 = 5.03 \times 10^{-2} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ at $T_2 = 289 \text{ K}$
 $k_1 = 6.71 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ at $T_1 = 333 \text{ K}$

$$\log \left(\frac{6.71}{5.03 \times 10^{-2}} \right) = \frac{E_a}{2.303 \times 8.314} \left(\frac{333 - 289}{333 \times 289} \right)$$

On solving we get, $E_a = 88.914 \text{ kJ}$

The rate constant at 305 K may be determined from the relation :

$$\log \frac{k_1}{k_2} = \frac{E_a}{2.303R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\log \left(\frac{k_1}{5.03 \times 10^{-2}} \right) = \frac{88.914}{2.303 \times 8.314} \left(\frac{1}{298} - \frac{1}{305} \right)$$

On solving we get, $k_1 = 0.35 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$

Problem : 18

A secondary alkyl halide (RX) is hydrolysed by alkali simultaneously by S_N1 and S_N2 pathways. A plot of

$-\frac{1}{[\text{RX}]} \frac{d[\text{RX}]}{dt}$ vs $[\text{OH}^-]$ is a straight line with slope equal to $1.0 \times 10^{-3} \text{ mol}^{-1} \text{ L min}^{-1}$ and intercept equal to $2.0 \times 10^{-3} \text{ min}^{-1}$. Calculate initial rate of consumption of RX when $[\text{RX}] = 0.5 \text{ M}$ and $[\text{OH}^-] = 1.0 \text{ M}$.

Sol. $1.5 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}$

For S_N1 pathway:

$$-\frac{d[\text{RX}]}{dt} = K_1[\text{RX}] \quad K_1 = 1^{\text{st}} \text{ order rate constant}$$

For S_N2 pathway:

$$-\frac{d[\text{RX}]}{dt} = K_2[\text{RX}][\text{OH}^-] \quad K_2 = 2^{\text{nd}} \text{ order rate constant}$$

Thus, the overall rate of consumption of RX is as given below:

$$-\frac{d[\text{RX}]}{dt} = K_1[\text{RX}] + K_2[\text{RX}][\text{OH}^-]$$

$$\text{or } -\frac{1}{[\text{RX}]} \frac{d[\text{RX}]}{dt} = K_1 + K_2[\text{OH}^-]$$

According to this equation as plot of $-\frac{1}{[\text{RX}]} \frac{d[\text{RX}]}{dt}$ vs $[\text{OH}^-]$ will be a straight line of the slope equal to K_2 and intercept equal to K_1 . Thus, from question.

$$K_1 = 2.0 \times 10^{-3} \text{ min}^{-1}$$

$$K_2 = 1.0 \times 10^{-3} \text{ min}^{-1} \text{ L min}^{-1}$$

$$\begin{aligned} \text{Thus, } -\frac{d[\text{RX}]}{dt} &= 2.0 \times 10^{-3} \times 0.5 + 1.0 \times 10^{-3} \times 0.5 \times 1 \\ &= 1 \times 10^{-3} + 0.5 \times 10^{-3} \\ &= 1.5 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1} \end{aligned}$$

Problem : 19

A polymerisation reaction is carried out at 2000 K and the same reaction is carried out at 4000 K with catalyst. The catalyst increases the potential barrier by 20 KJ but the rate of the reaction remains same. Find activation energy of the reaction.

(Assuming all other parameters to be same.)

Sol. 0020

$$k = Ae^{-E_a/R \times 2000} = Ae^{-\left(\frac{E_a + 20}{R \times 4000}\right)}$$

$$\frac{E_a}{R \times 2000} = \frac{(E_a + 20)}{R \times 4000}$$

$$2E_a = E_a + 20$$

$$E_a = 20 \text{ kJ}$$

Problem : 20

Consider the following first order parallel reaction. $2A \xrightarrow{3k} 3B$ and $2A \xrightarrow{5k} 5C$

The concentration of C after time t is :

Sol. $\frac{25}{16}[1 - e^{-16kt}]$

$$-\frac{1}{2} \frac{dA}{dt} = \frac{1}{3} \frac{dB}{dt} + \frac{1}{5} \frac{dC}{dt} = 3k[A] + 5k[A] = 8kA$$

$$-\frac{dA}{dt} = 8kA \times 2 = 16kA$$

$$A = A_0 e^{-16kt}$$

$$\frac{1}{3} \frac{dB}{dt} = 3kA, \quad \frac{dB}{dt} = 9kA = 9kA_0 e^{-16kt}$$

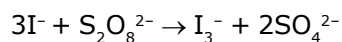
$$B = \frac{9}{16}[1 - e^{-16kt}]$$

Similarly

$$\frac{25}{16}[1 - e^{-16kt}]$$

Class Room Problems

Ex.1 The oxidation of iodide ion by peroxy disulphate ion is described by the equation :



(a) If $-\frac{\Delta[\text{S}_2\text{O}_8^{2-}]}{\Delta t} = 1.5 \times 10^{-3} \text{ Ms}^{-1}$ for a particular

time interval, what is the value of $-\frac{\Delta[\text{I}^-]}{\Delta t}$ for the same time interval ?

(b) What is the average rate of formation of SO_4^{2-} during that time interval ?

Sol. (a) 4.5×10^{-3} (b) 3×10^{-3}

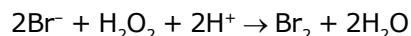
Ex.2 In the following reaction $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$ rate of formation of O_2 is 36 g min^{-1} ,

(A) What is rate of formation of H_2O ?

(B) What is rate of disappearance of H_2O_2 ?

Sol. (A) 40.5 (B) 76.5

Ex.3 The stoichiometric equation for the oxidation of bromide ions by hydrogen peroxide in acid solution is



Since the reaction does not occur in one stage, the rate equation does not correspond to this stoichiometric equation but is

$$\text{rate} = k[\text{H}_2\text{O}_2][\text{H}^+][\text{Br}^-]$$

(a) If the concentration of H_2O_2 is increased by a factor of 3, by what factor is the rate of consumption of Br^- ions increased ?

(b) If, under certain conditions, the rate of consumption of Br^- ions is $7.2 \times 10^{-3} \text{ mole dm}^{-3} \text{ s}^{-1}$, what is the rate of consumption of hydrogen peroxide ? What is the rate of production of bromine ?

(c) What is the effect on the rate constant k of increasing the concentration of bromide ions ?

(d) If by the addition of water to the reaction mixture the total volume were doubled, what would be the effect on the rate of change on change on the concentration of Br^- ? What would be the effect on the rate constant k ?

Sol. (a) 3 times (b) 3.6×10^{-3} (c) No. effect (d) 1/8 times, no. effect on k

Ex.4 For a reaction $2P + Q \rightarrow S$; following data were collected. Calculate the overall order of the reaction. Also find out the reaction rate constant.

	P(mole/L)	Q(mole/L)	Rate
1.	6×10^{-3}	1×10^{-3}	0.012
2.	6×10^{-3}	2×10^{-3}	0.024
3.	2×10^{-3}	1.5×10^{-3}	0.0024
4.	4×10^{-3}	1.5×10^{-3}	0.0096

Sol. $m = 2, n = 1$

Ex.5A 22.4 litre flask contains 0.76 mm of ozone at 25°C. Calculate

(i) the concentration of oxygen atom needed so that the reaction $O + O_3 \rightarrow 2O_2$ having rate constant equal to $1.5 \times 10^7 \text{ litre mol}^{-1} \text{ sec}^{-1}$ can proceed with a rate of $0.15 \text{ mol litre}^{-1} \text{ sec}^{-1}$.

(ii) the rate of formation of oxygen under this condition.

Sol. (i) 2.4×10^{-4} (ii) $2 \times 0.15 \text{ Ms}^{-1} = 0.30$

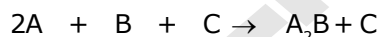
Ex.6 The rate of a reaction $A + B \rightarrow \text{products}$ is studied to give following data.

Initial [A] in mol/L	Initial [B] in mol/L	rate (mol/L/min)
0.01	0.01	0.005
0.02	0.01	0.010
0.01	0.02	0.005

What is the rate law? What is the half-life of A in the reaction

Sol. $K = 0.5, t_{1/2} = 1.386 \text{ min}, m = 1, n = 0$

Ex.7 For the reaction :



the rate = $k[A][B]^2$ with $k = 2.0 \times 10^{-6} \text{ M}^{-2} \text{ s}^{-1}$. Calculate the initial rate of the reaction when $[A] = 0.1 \text{ M}$, $[B] = 0.2 \text{ M}$ and $[C] = 0.8 \text{ M}$. If the rate of reverse reaction is negligible then calculate the rate of reaction after $[A]$ is reduced to 0.06 M .

Sol. $2.8 \times 10^{-9}, 3.88 \times 10^{-9}$

Ex.8 A & B are two different chemical species undergoing 1st order decomposition with half lives equal to 0.231 & 0.3465 sec respectively. If the initial conc.

of A & B are in the ratio 3 : 2. Calculate $\frac{[A]}{[B]}$ after three half lives of 'A'.

Sol. 0.375 : 0.5

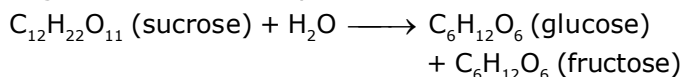
Ex.9A $\rightarrow B + C$

Time	T	∞
Volume of reagent	V_2	V_3

Reagent reacts with all A, B and C and have 'n' factors in the ratio of 1 : 2 : 3 with the reagent. Find k.

Sol. $K = 1/t \ln \frac{4V_3}{5V_3 - 5V_2}$

Ex.10 Inversion of sucrose is studied by measuring angle of rotation at any time t.



It is found that are $(r_0 - r_\infty) \propto a$ and $(r_t - r_\infty) \propto (a - x)$ where r_0 , r_t and r_∞ are the angle of rotation at the start, at the time t and at the end of the respectively. From the following values calculate the rate constant and time at which solution is optically inactive.

Time/ min.	0.0	46.0	∞
Rotation of Glucose & Fructose	24.1	10.0	-10.7

Sol. t = 104.43 min

Ex.11 The first order reaction :sucrose \longrightarrow Glucose + Fructose takes place at 308° K in 0.5 NHCl. At time zero the initial total rotation of the mixture is 32.4°. After 10 minutes the total rotation is 28.8°. If the rotation of sucrose per mole is 85°, that of glucose of the glucose is 74° and fructose is -86.04°. Calculate half life of the reaction.

Sol. 0.3 min

Ex.12 At room temperature (20°C) milk turns sour in about 65 hours. In a refrigerator at 3°C milk can be stored three times as long before its sours. Estimate : (a) Activation energy of the reaction that causes the souring of milk, (b) How long should it take milk to sour at 40°C.

Sol. 43.47 kJ/mole, 20.5 hr.

Ex.13 When the catalyst is removed from a reaction at 500°K the rate decreases upto 4 times and activation energy is increased by 20%. Find the ratio of velocity constants at temperature 320°K and 300°K in the absence of catalyst. Assume activation energy is independent to temperature.

Sol. $E_a = 34.6$, $\frac{k_2}{k_1} = 2.378$

COMPREHENSION

For a reaction, if effective rate constant k' is given

by $k = \frac{2k_2}{k_3} \left(\frac{k_1}{k_5} \right)^{1/5}$ where k_1, k_2, k_3, k_5 are rate constants for different steps of the reaction

Ex.14 The effective activation energy is

(a) $E_a = E_{a_2} - E_{a_3} + \frac{1}{5}E_{a_1} - \frac{1}{5}E_{a_5}$

(b) $E_a = E_{a_1} + E_{a_2} + E_{a_3} + E_{a_5}$

(c) $E_a = E_{a_1} + E_{a_2} - E_{a_3} - E_{a_5}$

(d) $E_a = E_{a_2} + E_{a_3} - E_{a_5} - E_{a_1}$

Sol.

Ex.15 The effective frequency factor

(a) $A' = \frac{A_2}{A_3} \left(\frac{A_1}{A_5} \right)^2$ (b) $A' = \left(\frac{2A_2}{A_3} \right) \left(\frac{A_1}{A_5} \right)^{1/5}$

(c) $A' = A_1 \times A_2 \times A_3 \times A_4$ (d) $A' = \left(\frac{A_1}{A_2} \right) \left(\frac{A_3}{A_5} \right)^{1/5}$

Sol.

Ex.16 Which one is correct ?

(a) $k' = 2 \frac{A_2 A_1^{1/5}}{A_3 A_5^{1/5}} \exp \left[\frac{-\{E_{a_2} + E_{a_3} + 1/5 E_{a_1} - 1/5 E_{a_5}\}}{RT} \right]$

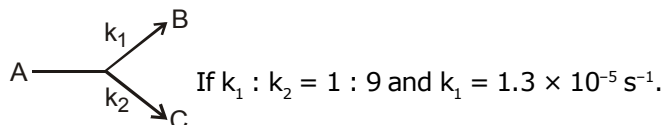
(b) $k' = 2 \frac{A_2 A_1^{1/5}}{A_3 A_5^{1/5}} \exp \left[\frac{-\{E_{a_1} + E_{a_3} + 1/5 E_{a_2} - 1/5 E_{a_5}\}}{RT} \right]$

(c) $k' = 2 \frac{A_2 A_5^{1/5}}{A_3 A_1^{1/5}} \exp \left[\frac{-\{E_{a_1} + E_{a_2} + E_{a_3} + E_{a_5}\}}{RT} \right]$

(d) none of these.

Sol.

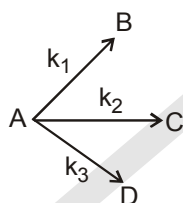
Ex.17 A certain organic compound A decomposes by two parallel first order mechanism



Calculate the concentration ratio of C to A, if an experiment is started with only A and allowed to run for one hour.

Sol. 0.537

Ex.18 For a parallel first order reaction

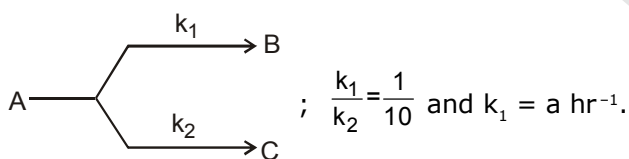


where $k_1 = x \text{ hr}^{-1}$ and $k_1 : k_2 : k_3 = 1 : 10 : 100$.

Calculate $\frac{[B]}{[A_t]}$, $\frac{[C]}{[A_t]}$ and $\frac{[D]}{[A_t]} = \dots\dots\dots$

Sol. $K_{\text{eff}} = 111 k_1 \quad \frac{A_0}{A} = \frac{A+B+C+D}{A} = e^{111k_1 t}$

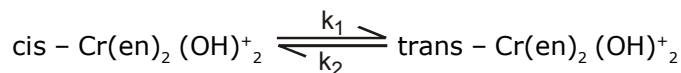
Ex.19 An organic compound A decomposes following two parallel first order mechanisms :



Calculate the concentration ratio of C to A after one hour from the start of the reaction, assuming only A was present in beginning.

Sol. $\frac{10}{11}(e^{11x} - 1)$

Ex.20. The reaction



is first order in both directions. At 25°C the equilibrium constant is 0.16 and the rate constant k_1 is $3.3 \times 10^{-4} \text{ s}^{-1}$. In an experiment starting with the pure cis form, how long would it take for half the equilibrium amount of the trans isomer to be formed ?

Sol. 4.83 min.

Ex.21 Two reactions (i) $A \rightarrow \text{products}$ (ii) $B \rightarrow \text{products}$, follow first order kinetics. The rate of the reaction (i) is doubled when the temperature is raised from 300 K to 310 K. The half life for this reaction at 310 K is 30 minutes. At the same temperature B decomposes twice as fast as A. If the energy of activation for the reaction (ii) is half that of reaction (i), calculate the rate constant of the reaction (ii) at 300 K.

Sol. 0.0327 min^{-1}

Ex.22 For a reaction $A_2 + B_2 \rightarrow 2AB$, evaluate the energy of activation from the following data:

$$T \text{ (in K)} \quad \frac{1}{T} \text{ (K}^{-1}\text{)} \quad \log_{10} K$$

$$500 \quad 2 \times 10^{-3} \quad 3.0$$

$$200 \quad 5 \times 10^{-3} \quad 2.0$$

Sol. $E_a = 6.382 \text{ kJ}$

Sol. $6 \times 10^4 \text{ J}, 9.3 \times 10^4 \text{ J}$

Ex.25 A first order reaction $A \rightarrow B$ requires activation energy of 70 kJ mol^{-1} . When a 20% solution of A was kept at 25°C for 20 minute, 25% decomposition took place. What will be the percent decomposition in the same time in a 30% solution maintained at 40°C ? Assume that activation energy remains constant in this range of temperature.

Sol. 67.2%

Ex.23 A reaction proceeds five times more at 60°C as it does at 30°C . Estimate energy of activation.

Sol. 45 kJ

Ex.26 At 380°C , the half life period for the first order decomposition of H_2O_2 is 360 min. The energy of activation of the reaction is 200 kJ mol^{-1} . Calculate the time required for 75% decomposition at 450°C .

Sol. 20.4

Ex.24 For the reaction $A \rightleftharpoons B$, ΔE for the reaction is $-33.0 \text{ kJ mol}^{-1}$. Calculate :

(a) equilibrium constant K_c for the reaction at 300 K

(b) If E_f and E_b are in the ratio 20 : 31, calculate E_f , E_b at 300 K. Assuming pre-exponential factor same for forward and backward reactions.

Ex.27 The energy of activation for a reaction is 100 kJ mol^{-1} . Presence of a catalyst lowers the energy of activation by 75%. What will be effect on rate of reaction at 20°C ; other things being equal?

Sol. $2.35 \times 10^{13} \text{ time} = e^{30.79}$

Ex.28 (a) The reaction A proceeds in parallel chan-

nels A $\begin{matrix} \nearrow B \\ \searrow C \end{matrix}$ Although the $A \rightarrow C$ branch is thermodynamically more favorable than the branch $A \rightarrow B$, the product B may dominate in quantity over C. Why may this be so ?

(b) In the above problem, suppose the half life values for the two branches are 60 minutes and 90 minutes, what is the overall half-life value?

Sol.

Ex.29 Deduce rate law expressions for the conversion of H_2 and I_2 to HI at 400°C corresponding to each of the following mechanisms :

(a) $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$ (one step)

(b) $\text{I}_2 \rightleftharpoons 2\text{I}$

$2\text{I} + \text{H}_2 \rightarrow 2\text{HI}$ (slow)

(c) $\text{I}_2 \rightleftharpoons 2\text{I}$

$\text{I} + \text{H}_2 \rightleftharpoons \text{IH}_2$

$\text{IH}_2 + \text{I} \rightarrow 2\text{HI}$ (slow)

(d) Can the observed rate law expression rate = $k[\text{H}_2][\text{I}_2]$ distinguish among these mechanisms ?

(e) If it is known that ultraviolet light causes the reaction of H_2 and I_2 to proceed at 200°C with the same rate law expression, which of these mechanisms becomes most improbable ? Are any of these mechanisms proved ?

Sol. No, Mechanism 'a' is wrong.

Ex.30 Hydrolysis of methyl acetate in aqueous solution has been studied by titrating the liberated acetic acid against sodium hydroxide. The concentration of the ester at different times is given below.

t/min	0	30	60	90
C/mol L ⁻¹	0.8500	0.8004	0.7538	0.7096

What is the value of k' in this equation if

Rate = $k' [\text{CH}_3\text{COOCH}_3][\text{H}_2\text{O}]$

Ans. $3.64 \times 10^{-5} \text{ M}^{-1} \text{ min}^{-1}$

EXERCISE – I**OBJECTIVE PROBLEMS (JEE MAIN)**

1. The rate of a reaction is expressed in different ways as follows :

$$+\frac{1}{2} \frac{d[C]}{dt} = -\frac{1}{3} \frac{d[D]}{dt} = +\frac{1}{4} \frac{d[A]}{dt} = -\frac{d[B]}{dt}$$

The reaction is :

- (A) $4A + B \rightarrow 2C + 3D$ (B) $B + 3D \rightarrow 4A + 2C$
 (C) $A + B \rightarrow C + D$ (D) $B + D \rightarrow A + C$

Sol.

2. The rate constant for the forward reaction $A(g) \rightleftharpoons 2B(g)$ is $1.5 \times 10^{-3} \text{ s}^{-1}$ at 100 K. If 10^{-5} moles of A and 100 moles of B are present in a 10 litre vessel at equilibrium then rate constant for the backward reaction at this temperature is

- (A) $1.50 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$ (B) $1.5 \times 10^{11} \text{ L mol}^{-1} \text{ s}^{-1}$
 (C) $1.5 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ (D) 1.5×10^{-11}

Sol.

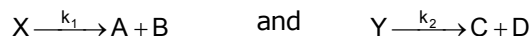
3. Reaction $A + B \rightarrow C + D$ follow's following rate law : $\text{rate} = k[A]^{+1/2}[B]^{1/2}$. Starting with initial conc. of 1 M of A and B each, what is the time taken for concentration of A of become 0.25 M.

Given : $k = 2.303 \times 10^{-3} \text{ sec}^{-1}$.

- (A) 300 sec (B) 600sec
 (C) 900 sec (D) none of these

Sol.

4. Consider the following first order competing reactions :



if 50% of the reaction of X was completed when 96% of the reaction of Y was completed, the ratio of their

rate constants $\left(\frac{k_2}{k_1}\right)$ is

- (A) 4.06 (B) 0.215 (C) 1.1 (D) 4.65

Sol.

5. Units of rate constant for first and zero order reactions in terms of molarity (M) are respectively.

- (A) sec^{-1} , M sec^{-1} (B) sec^{-1} , M
 (C) M sec^{-1} , sec^{-1} (D) M, sec^{-1}

Sol.

6. For the reaction $A + B \rightarrow C$; starting with different initial concentration of A and B, initial rate of reaction were determined graphically in four experiments.

S.NO.	[A] ₀ /M (Initial conc.)	[B] ₀ /M (Initial conc.)	rate / (M sec ⁻¹)
1	1.6×10^{-3}	5×10^{-2}	10^{-3}
2	3.2×10^{-3}	5×10^{-2}	4×10^{-3}
3	1.6×10^{-3}	10^{-1}	2×10^{-3}
4	3.2×10^{-3}	10^{-1}	8×10^{-3}

Rate law for reaction from above data is

- (A) $r = k[A]^2[B]^2$ (B) $r = k[A]^2[B]$
 (C) $r = k[A][B]^2$ (D) $r = k[A][B]$

Sol.

7. For a reaction $pA + qB \rightarrow \text{products}$, the rate law expression is $r = k[A]^p[B]^q$, then :

- (A) $(p + q) < (1 + m)$
 (B) $(p + q) > (1 + m)$
 (C) $(p + q)$ may or may not be equal to $(1 + m)$
 (D) $(p + q) = (1 + m)$

Sol.

8. In the reaction : $A + 2B \rightarrow 3C + D$, which of the following expression does not describe changes in the conc. of various species as a function of time :

- (A) $\{-d[C]/dt\} = \{3/2d[B]/dt\}$
 (B) $\{3d[D]/dt\} = \{d[C]/dt\}$
 (C) $\{3d[B]/dt\} = \{-2d[C]/dt\}$
 (D) $\{2d[B]/dt\} = \{d[A]/dt\}$

Sol.

9. For the reaction, $2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$ the rate expression can be written in the following ways : $\{d[N_2]/dt\} = k_1[NO][H_2]$; $\{d[H_2O]/dt\} = k[NO][H_2]$; $\{-d[NO]/dt\} = k'_1$, $[NO][H_2]$; $\{-d[H_2]/dt\} = k''_1[NO][H_2]$. The relationship between k , k_1 , k'_1 and k''_1 is :

- (A) $k = k_1 = k'_1 = k''_1$ (B) $k = 2k_1 = k'_1 = k''_1$
 (C) $k = 2k'_1 = k_1 k''_1$ (D) $k = k_1 = k'_1 = k_1 k''_1$

Sol.

10. At certain temperature, the half life period in the thermal decomposition of a gaseous substance as follows :

P (mmHg)	500	250
$t_{1/2}$ (in min)	235	950

Find the order of reaction [Given $\log(23.5) = 1.37$; $\log(95) = 1.97$]

- (A) 1 (B) 2 (C) 2.5 (D) 3

Sol.

11. A first order reaction is 50% completed in 20 minutes at 27°C and in 5 min at 47°C . The energy of activation of the reaction is

- (A) 43.85 kJ/mol (B) 55.14 kJ/mol
 (C) 11.97 kJ/mol (D) 6.65 kJ/mol

Sol.

12. For the first order reaction $A \rightarrow B + C$, carried out at 27°C if $3.8 \times 10^{-16}\%$ of the reactant molecules exists in the activated state, the E_a (activation energy) of the reaction is

- (A) 12 kJ/mole (B) 831.4 kJ/mole
 (C) 100 KJ/mole (D) 88.57 kJ/mole

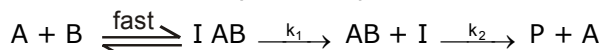
Sol.

13. The rate constant, the activation energy and the Arrhenius parameter (A) of a chemical reaction at 25°C are $3.0 \times 10^{-4} \text{ s}^{-1}$, $104.4 \text{ kJ mol}^{-1}$ and $6.0 \times 10^{-4} \text{ s}^{-1}$ respectively. The value of the rate constant at $T \rightarrow \infty$ is

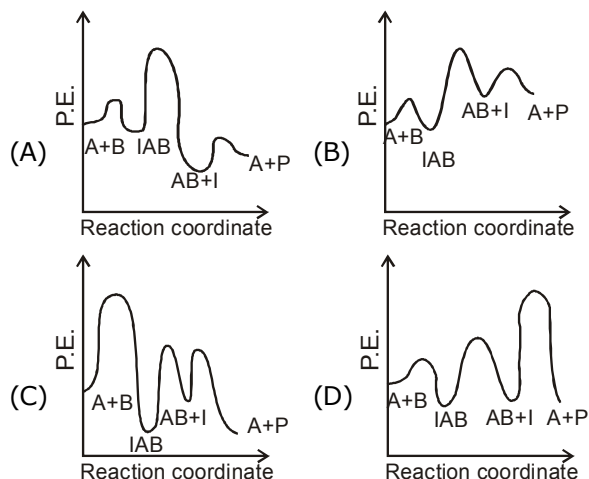
- (A) $2.0 \times 10^{18} \text{ s}^{-1}$ (B) $6.0 \times 10^{14} \text{ s}^{-1}$
 (C) infinity (D) $6 \times 10^{-4} \text{ s}^{-1}$

Sol.

14. The following mechanism has been proposed for the exothermic catalyzed complex reaction.

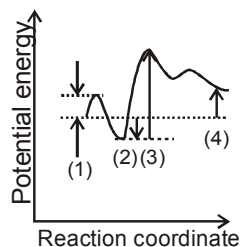


If k_1 is much smaller than k_2 . The most suitable qualitative plot of potential energy (P.E.) versus reaction coordinate for the above reaction.



Sol.

15. Choose the correct set of identifications.



- | (1) | (2) | (3) | (4) |
|---|---|---|---|
| (A) ΔE for $E + S \rightarrow ES$ | E_a for $ES \rightarrow EP$ | $\Delta E_{\text{overall}}$ for $S \rightarrow P$ | E_a for $EP \rightarrow E + P$ |
| (B) E_a for $E + S \rightarrow ES$ | ΔE for $E + S \rightarrow ES$ | E_a for $ES \rightarrow EP$ | $\Delta E_{\text{overall}}$ for $S \rightarrow P$ |
| (C) E_a for $ES \rightarrow EP$ | E_a for $EP \rightarrow E + P$ | $\Delta E_{\text{overall}}$ for $S \rightarrow P$ | ΔE for $EP \rightarrow E + P$ |
| (D) E_a for $E + S \rightarrow ES$ | E_a for $ES \rightarrow EP$ | E_a for $EP \rightarrow E + P$ | $\Delta E_{\text{overall}}$ for $S \rightarrow P$ |
| (E) ΔE for $E + S \rightarrow ES$ | $\Delta E_{\text{overall}}$ for $S \rightarrow P$ | ΔE for $EP \rightarrow E + P$ | E_a for $EP \rightarrow E + P$ |

Sol.

16. Consider $A \xrightleftharpoons[B.R.]{F.R.} B + \text{heat}$. If activation energy for forward reaction is 100 kJ/mole then activation energy for backward reaction and heat of reaction is :

- (A) 100, 200 (B) 80, 20
(C) 120, 220 (D) 140, 40

Sol.

17. In a reaction, the threshold energy is equal to :

- (A) Activation energy + normal energy of reactants
(B) Activation energy - normal energy of reactants
(C) Activation energy
(D) Normal energy of reactants.

Sol.

18. The first order rate constant k is related to temperature as $\log k = 15.0 - (10^6/T)$. Which of the following pair of value is correct ?

- (A) $A = 10^{15}$ and $E = 1.9 \times 10^4$ KJ
(B) $A = 10^{-15}$ and $E = 40$ KJ
(C) $A = 10^{15}$ and $E = 40$ KJ
(D) $A = 10^{-15}$ and $E = 1.9 \times 10^4$ KJ

Sol.

19. When a graph between $\log K$ and $1/T$ is drawn a straight line is obtained. The temperature at which line cuts y-axis and x-axis.

- (A) 0, $E_a/2.303 R \log A$ (B) ∞ , $E_a/(R \ln A)$
(C) 0, $\log A$ (D) None of these

Sol.

20. The rate constant, the activation energy and the frequency factor of a chemical reaction at 25°C are $3.0 \times 10^{-2} \text{ s}^{-1}$, $104.4 \text{ kJ mol}^{-1}$ and $6.0 \times 10^{14} \text{ s}^{-1}$ respectively.

The value of the rate constant as $T \rightarrow \infty$ is :

- (A) $2.0 \times 10^{18} \text{ s}^{-1}$ (B) $6.0 \times 10^{14} \text{ s}^{-1}$
(C) infinity (D) $3.6 \times 10^{30} \text{ s}^{-1}$

Sol.

21. The rate data for the net reaction at 25°C for the reaction $\text{X} + 2\text{Y} \rightarrow 3\text{Z}$ are given below :

$[\text{X}_0]$ $[\text{Y}_0]$ Time required for $[\text{Z}]$ to increase by 0.005 mol per litre.

0.01	0.01	72 sec
0.02	0.005	36 sec
0.02	0.01	18 sec

The initial rate (as given by Z) is :

- (A) First order in both X and Y
(B) Second order in X and first order in Y
(C) First order in X and second order in Y
(D) None of the above

Sol.

22. The rate of production of NH_3 in $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$ is 3.4 kg min^{-1} . The rate of consumption of H_2 is :

- (A) 5.1 kg min^{-1} (B) 0.01 kg sec^{-1}
(C) 0.6 kg hr^{-1} (D) None of these

Sol.

23. For a given reaction of first order it takes 20 min. for the conc. to drop from 1.0 M to 0.60 M. The time required for the conc. to drop from 0.60 M to 0.36 M will be :

- (A) more than 20 min (B) 20 min
(C) less than 30 min (D) cannot tell.

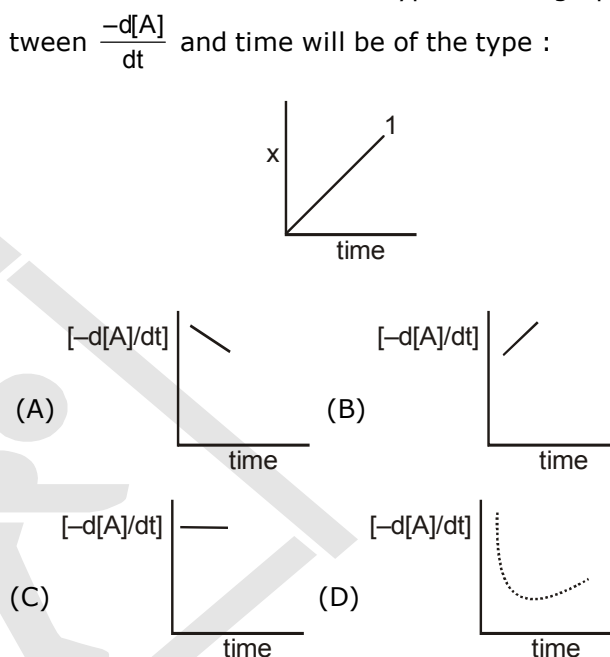
Sol.

24. For a first order reaction, the concentration of reactant :

- (A) is independent of time
(B) varies linearly with time
(C) varies exponentially with time (D) None

Sol.

25. Graph between conc. of the product and time of the reaction $\text{A} \rightarrow \text{B}$ is of the type. Hence graph between $\frac{-d[\text{A}]}{dt}$ and time will be of the type :



Sol.

26. Mathematical representation for $t_{1/4}$ life for first order reaction is over is given by :

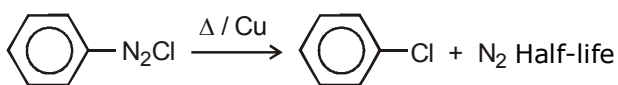
- (A) $t_{1/4} = [(2.303)/(K)] \log 4$
(B) $t_{1/4} = [(2.303)/(K)] \log 3$
(C) $t_{1/4} = [(2.303)/(K)] \log(4/3)$
(D) $t_{1/4} = [(2.303)/(K)] \log(3/4)$

Sol.

27. For a reaction $A \rightarrow \text{Products}$, the conc. of reactant $C_0, aC_0, a^2C_0, a^3C_0, \dots$ after time interval $0, t, 2t, \dots$ where 'a' is constant. Then :

- (A) reaction is of 1st order and $K = (1/t) \ln a$
 (B) reaction is of 2nd order and $K = (1/tC_0)(1 - a)/a$
 (C) reaction is of 1st order and $K = (1/t) \ln (1/a)$
 (D) reaction is of zero order and $K = \{(1 - a)\}C_0/t$

Sol.

28.  Half-life is independent of conc. of A. After 10 minutes volume N_2 gas is 10 L and after complete reaction 50 L. Hence rate constant in min^{-1} :

- (A) $(2.303/10) \log 5$ (B) $(2.303/10) \log 1.25$
 (C) $(2.303/10) \log 2$ (D) $(2.303/10) \log 4$

Sol.

29. A reaction $2A + B \xrightarrow{k} C + D$ is first order with respect to A and 2nd order with respect to B. Initial conc. ($t = 0$) of A is C_0 while B is $2C_0$. If at $t = 30$ minutes the conc. of C is $C_0/4$ then rate at $t = 30$ minutes is :

- (A) $\frac{7C_0^3k}{16}$ (B) $\frac{27C_0^3k}{32}$ (C) $\frac{247C_0^3k}{64}$ (D) $\frac{49kC_0^3}{32}$

Sol.

30. In acidic medium the rate of reaction between $(\text{BrO}_3)^-$ and Br^- ions is given by the expression, $-\frac{d(\text{BrO}_3^-)}{dt} = K[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$ It means :

- (A) Rate constant of overall reaction is 4 sec^{-1}
 (B) Rate of reaction is independent of the conc. of acid
 (C) The change in pH of the solution will not affect the rate
 (D) Doubling the conc. of H^+ ions will increase the reaction rate by 4 times.

Sol.

31. The decomposition of a gaseous substance (A) to yield gaseous products (B), (C) follows first order kinetics. If initially only (A) is present and 10 minutes after the start of the reaction the pressure of (A) is 200 mm Hg and that of over all mixture is 300 mm Hg, then the rate constant for $2A \rightarrow B + 3C$ is

- (A) $(1/600) \ln 1.25 \text{ sec}^{-1}$ (B) $(2.303/10) \log 1.5 \text{ min}^{-1}$
 (C) $(1/10) \ln 1.25 \text{ sec}^{-1}$ (D) None of these

Sol.

32. For a certain reaction of order 'n' the time for half change $t_{1/2}$ is given by $t_{1/2} = [(2 - \sqrt{2})/K] \times C_0^{1/2}$, where K is rate constant and C_0 is the initial concentration. The value of n is :

- (A) 1 (B) 2 (C) 0 (D) 0.5

Sol.

33. Two first order reaction have half life in the ratio 3 : 2. Calculate the ratio of time intervals $t_1 : t_2$. The time t_1 and t_2 are the time period for 25% and 75% completion for the first and second reaction respectively :

- (A) 0.311 : 1 (B) 0.420 : 1
 (C) 0.273 : 1 (D) 0.119 : 1

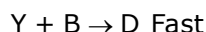
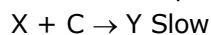
Sol.

34. A reaction proceeds in three stages, The first stage is a slow second order reaction, the second stage is fast and of first order, the third stage is fast and is a third order reaction. The overall order of the reaction is :

- (A) First order (B) Second order
(C) Third order (D) Zero order.

Sol.

35. A reaction of the type $A + 2B + C \rightarrow D$ occurs by following mechanism

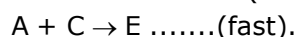
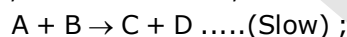


What is the order of the reaction :

- (A) 1 (B) 2 (C) 3
(D) Non determinable

Sol.

36. Following mechanism has been proposed for a reactions, $2A + B \rightarrow D + E$;



The rate law expression for the reaction is :

- (A) $r = K[A]^2$ (B) $r = K[A]^2[B]$
(C) $R = K[A]^2$ (D) $r = K[A][B]$

Sol.

37. For the reaction $H_2 + I_2 \xrightleftharpoons[k_2]{k_1} 2HI$. The rate law expression is :

- (A) $[(+1/2) d[HI]/dt] = k_1 [H_2] [I_2]$
(B) $[(+1/2) d[HI]/dt] = \{k_1 [HI]^2 / k_2 [H_2][I_2]\}$
(C) $[(+1/2) d[HI]/dt] = k_1 [H_2][I_2] - k_2 [HI]^2$
(D) $[(+1/2) d[HI]/dt] = k_1 k_2 [H_2][I_2]$

Sol.

38. A substance undergoes first order decomposition. The decomposition follows two parallel first order reactions as : and $K_1 = 1.26 \times 10^{-4} \text{ sec}^{-1}$; $K_2 = 3.8 \times 10^{-5} \text{ sec}^{-1}$. The percentage distribution of B and C are

- (A) 80% B and 20% C (B) 76.83% B and 23.17% C
(C) 90% B and 10% C (D) 60% B and 40% C

Sol.

39. For $2A \xrightleftharpoons[k_{-1}]{k_1} B + 3C$, $2C \xrightarrow{k_2} 3D$. Which of the following is correct :

- (A) $d[C]/dt = 3k_1[A]^2 - 3k_{-1}[B][C]^3 - 2K_2[C]^2$
(B) $d[B]/dt = k_1[A]^2$
(C) $d[A]/dt = 2K_{-1}[B][C]^3 - 2K_1[B][C]^3$
(D) None.

Sol.

40. For $2A \xrightarrow{k_1} B \xrightarrow{k_2} 3C$. $k_1 = 2 \times 10^{-4} \text{ sec}^{-1}$ and $k_2 = 3 \times 10^{-4} \text{ l/mol-sec}$. $\{d[B]/dt\}$ equal to:

- (A) $k_1[A] - k_2[B]$ (B) $k_1[A]^2 - k_2[B]$
(C) $k_1[A] - k_2[B]^2$ (D) $k_1[A]^2 - k_2[C]^3$

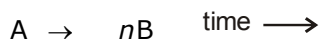
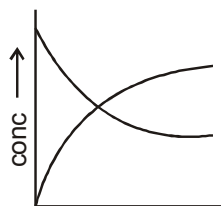
Sol.

41. For the reaction : $A + 2B \rightleftharpoons AB_2$; the rate of forward reaction is $\frac{dx}{dt} = 1 \times 10^5 [A][B]^2 - 1 \times 10^4 [AB_2]$. The rate constants for forward and backward reactions are :

- (A) $1 \times 10^5 \text{ L}^2 \text{ m}^{-2} \text{ s}^{-1}$, $1 \times 10^4 \text{ sec}$
(B) $1 \times 10^5 \text{ sec}^{-1}$, $1 \times 10^4 \text{ L}^2 \text{ m}^{-2} \text{ s}^{-1}$
(C) $1 \times 10^5 \text{ L}^2 \text{ m}^{-2} \text{ s}^{-1}$, $1 \times 10^4 \text{ sec}^{-1}$
(D) $1 \times 10^5 \text{ L m}^{-1} \text{ s}^{-1}$, $1 \times 10^4 \text{ sec}$

Sol.

42. At the point of intersection of the two curves shown for the reaction



the concentration of B is given by :

- (A) $\frac{nA_0}{2}$ (B) $\frac{A_0}{n-1}$ (C) $\frac{nA_0}{n+1}$ (D) $\frac{(n-1)}{(n+1)}A_0$

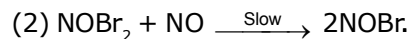
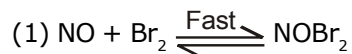
Sol.

43. For a hypothetical reaction $aA + bB \rightarrow \text{Product}$, the rate law is : rate = $K[A]^x[B]^y$. then :

- (A) $(a + b) = (x + y)$ (B) $(a + b) < (x + y)$
 (C) $(a + b) > (x + y)$ (D) Any of these

Sol.

44. For the reaction : $2NO + Br_2 \rightleftharpoons 2NOBr$; the mechanism is given in two steps :



The rate expression for the reaction is :

- (A) $r = K[NO]^2[Br_2]$ (B) $r = K[NO][Br_2]$
 (C) $r = K[NO][Br_2]^2$ (D) $r = K[NOBr_2]$

Sol.

45. For a gaseous reaction, the rate is expressed in terms of $\frac{dP}{dt}$ in place of $\frac{dC}{dt}$ or $\frac{dn}{dt}$, where C is concentration, n is number of moles and 'P' is pressure of reactant. The three are related as :

$$(A) \left[\frac{dP}{dt} \right] = \frac{RT}{V} \left[\frac{dn}{dt} \right] = \left[\frac{dC}{dt} \right]$$

$$(B) \frac{1}{RT} \left[\frac{dP}{dt} \right] = \frac{1}{V} \left[\frac{dn}{dt} \right] = \left[\frac{dC}{dt} \right]$$

$$(C) \left[\frac{dP}{dt} \right] = \left[\frac{dn}{dt} \right] = \left[\frac{dC}{dt} \right] \quad (D) \text{ None of these}$$

Sol.

46. For a chemical reaction : $A \rightarrow \text{Product}$, the rate of disappearance of A is given by :

$\frac{-dC_A}{dt} = K_1 \frac{C_A}{1 + K_2 C_A}$. At low C_A , the order of reaction and rate constants are respectively :

- (A) I, $\frac{K_1}{K_2}$ (B) I, K_1 (C) II, $\frac{K_1}{K_2}$ (D) II, $\frac{K_1}{K_1 + K_2}$

Sol.

47. For a reversible reaction, $A + B \rightleftharpoons C + D$; $\Delta H = -A \text{ kcal}$. If energy of activation for the forward reaction is B kcal, the energy of activation for backward reaction in kcal is :

- (A) $-A + B$ (B) $A + B$ (C) $A - B$ (D) $-A - B$

Sol.

48. The reaction $A(g) \longrightarrow B(g) + 2C(g)$ is a first order reaction with rate constant $3465 \times 10^{-6} \text{ s}^{-1}$. Starting with 0.1 mole of A in 2 litre vessel, find the concentration of A after 200 sec., when the reaction is allowed to take place at constant pressure and temperature.

- (A) 0.05 M (B) 0.025 M (C) 0.0125 M
(D) None of these

Sol.

49. How much faster would a reaction proceed at 25°C than at 0°C if the activation energy is 2 cal :

- (A) 2 times (B) 16 times
(C) 11 times (D) Almost at same speed

Sol.

50. The temperature coefficient of reaction I is 2 and reaction II is 3. Both have same speed at 25°C and show I order kinetics. The ratio of rates of reactions of these two at 75°C is :

- (A) 7.6 (B) 5.6 (C) 6.6 (D) 8.6

Sol.

EXERCISE – II**OBJECTIVE PROBLEMS (JEE ADVANCED)****Single correct**

1. The reaction $\text{CH}_3 - \text{CH}_2 - \text{NO}_2 + \text{OH}^- \rightarrow \text{CH}_3 - \text{CH} - \text{NO}_2 + \text{H}_2\text{O}$ obeys the rate law for pseudo first order kinetics in the presence of a large excess of hydroxide ion. If 1% of nitro ethane undergoes reaction in half a minute when the reactant concentration is 0.002 M, What is the pseudo first order rate constant ?

- (A) 0.02 min^{-1} (B) 0.05 min^{-1}
(C) 0.01 min^{-1} (D) 0.04 min^{-1}

Sol.

2. Decomposition of H_2O_2 is a first order reaction. A solution of H_2O_2 labelled as "16.8 V" was left open. Due to this, some H_2O_2 decomposed. To determine the new volume strength after 2.303 hours, 20 mL of this solution was diluted to 100 mL. 25 mL of this diluted solution was titrated against 37.5 mL of 0.02 M KMnO_4 solution under acidic conditions [Given : STP is 1 atm and 273 K] Calculate the rate constant (in hr^{-1}) for decomposition of H_2O_2 .

- (A) 0.6 (B) 0.5 (C) 0.4 (D) 0.8

Sol.

3. The reaction $\text{A} \xrightarrow{\text{OH}^-} \text{B}$, obeys the rate law for pseudo first order kinetics in the presence of a large excess of hydroxide ion. If 90% of A undergoes reaction in half a minute when the reactant concentration is 0.002 M, What is the pseudo first order rate constant in min^{-1}

- (A) 4.61 (B) 2.61 (C) 3.61 (D) 5.61

Sol.

4. $\text{A} \xrightarrow{\text{K}} \text{B}$, $t_{1/2} = 10 \text{ min}$

$3\text{A} \longrightarrow \text{C}$

Both reaction have same rate constant and each occurring following first order kinetics.

Choose the correct option for second reaction.

- (A) $t_{1/2} = 10/3 \text{ min}$ (B) $t_{1/2} = 30 \text{ min}$
(C) $t_{1/2} = 10 \text{ min}$ (D) Data insufficient

Sol.

5. The gas phase decomposition (in closed container)

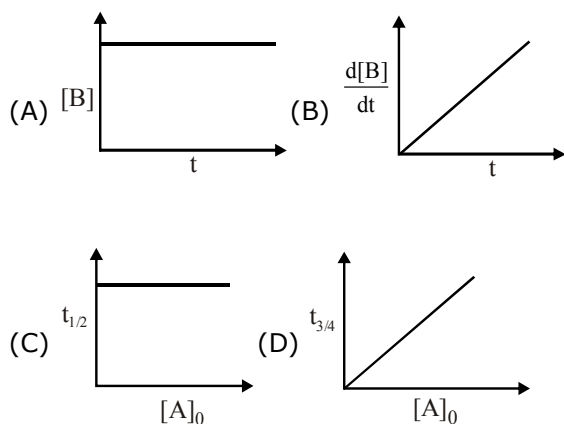


Follows the first order rate law. At a given temperature specific reaction rate is $7.5 \times 10^{-3} \text{ s}^{-1}$. The initial pressure of A is 0.1 atm. Calculate the time of decomposition of A so that the total pressure becomes 0.15 atm. ($\log 1.4925 = 0.1739$).

- (A) 66.6 sec (B) 22.24 sec
(C) 53.4 sec (D) None of these

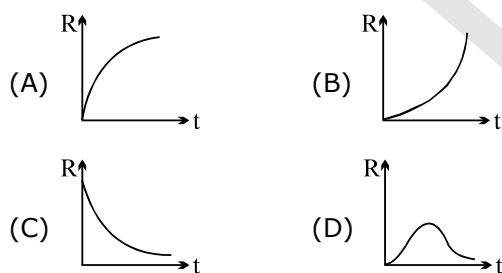
Sol. C

6. Which graph represents zero order reaction $[A(g) \rightarrow B(g)]$:



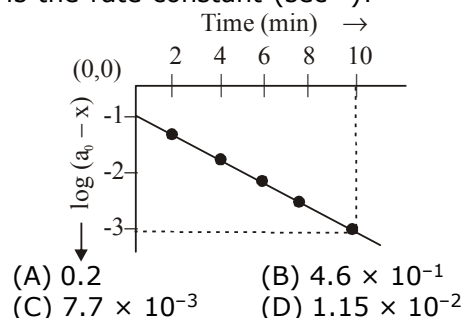
Sol.

7. If decomposition reaction $A(g) \rightarrow B(g)$ follows first order kinetics then the graph of rate of formation (R) of B against time t will be



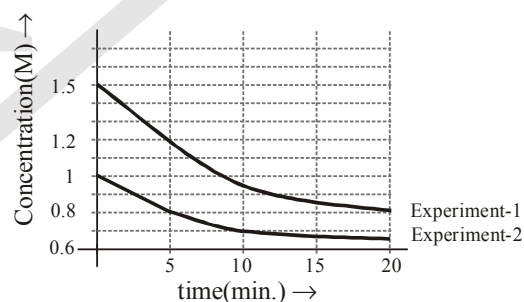
Sol.

8. For the first order decomposition of $SO_2Cl_2(g)$, $SO_2Cl_2(g) \rightarrow SO_2(g) + Cl_2(g)$ a graph of $\log(a_0 - x)$ vs t is shown in figure. What is the rate constant (sec^{-1})?



Sol.

9. The variation of concentration of A with time in two experiments starting with two different initial concentration of A is given in the following graph. The reaction is represented as $A(aq) \rightarrow B(aq)$. What is the rate of reaction (M/min) when concentration of A in aqueous solution was $1.8 M$?



- (A) $0.08 M \text{ min}^{-1}$ (B) $0.036 M \text{ min}^{-1}$
(C) $0.13 M \text{ min}^{-1}$ (D) $1 M \text{ min}^{-1}$

Sol.

10. SO_3 gas is entering the environment at a constant rate of 6.93×10^{-6} gm/L/day due to the emission of polluting gases from thermal power plant, but at the same time it is decomposing & following first order kinetics with half life of 100 days.

Based on above information select the true statement(s).

(A) Concentration of SO_3 in Kota is 1.25×10^{-5} M (Assume SO_3 present in air reaches steady state)

(B) If 10^3 L of air is passed through 1 L pure water (assuming all SO_3 to be dissolved in it) & resulting solution is titrated against 1 N NaOH solution, 15 ml is required to reach end point.

(C) An industry is manufacturing H_2SO_4 at the rate of 980 kg per day with the use of SO_3 in air it should use 8×10^5 Litre air /day.

(D) If SO_3 emission is stopped then after 1000 days its concentrations will reduce to $\approx 1.2 \times 10^{-8}$ M.

Sol.

11. For the reaction $A \rightarrow B$, the rate law expression

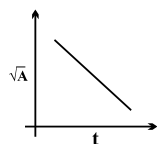
is $-\frac{d[A]}{dt} = k[A]^{1/2}$. If initial concentration of $[A]$ is

$[A]_0$, then

(A) The integrated rate expression is $k =$

$$\frac{2}{t}(A_0^{1/2} - A^{1/2})$$

(B) The graph of \sqrt{A} Vs t will be



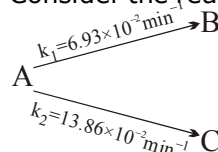
(C) The half life period $t_{1/2} = \frac{K}{2[A]_0^{1/2}}$

(D) The time taken for 75% completion of reaction

$$t_{3/4} = \frac{\sqrt{[A]_0}}{k}$$

Sol.

12. Consider the reaction,



A, B and C all are optically active compound. If optical rotation per unit concentration of A, B and C are 60° , -72° , 42° and initial concentration of A is 2 M then select write statement(s).

(A) Solution will be optically active and dextro after very long time

(B) Solution will be optically active and levo after very long time

(C) Half life of reaction is 15 min

(D) After 75% conversion of A into B and C angle of rotation of solution will be 36° .

Sol.

REASONING TYPE

Directions : Read the following questions and choose

(A) If both the statements are true and statement-2 is the correct explanation of statement-1.

(B) If both the statements are true and statement-2 is not the correct explanation of statement-1.

(C) If statement-1 is True and statement-2 is False.

(D) If statement-1 is False and statement-2 is True.

Assertion & Reasoning type questions

13. Statement-1 : A fractional order reaction must be a complex reaction.

Statement-2 : Fractional order of RDS equals to
(A) (A) (B) (B) (C) (C) (D) (D)

Sol.

14. Statement-1 : The time of completion of reactions of type $A \rightarrow \text{product}$ (order < 1) may be determined.

Statement-2 : Reactions with order ≥ 1 are either too slow or too fast and hence the time of completion can not be determined.

(A) (A) (B) (B) (C) (C) (D) (D)

Sol.

15. Statement-1 : Temperature coefficient of an one step reaction may be negative.

Statement-2 : The rate of reaction having negative order with respect to a reactant decreases with the increase in concentration of the reactant.

(A) (A) (B) (B) (C) (C) (D) (D)

Sol.

16. Statement-1 : The overall rate of a reversible reaction may decrease with the increase in temperature.

Statement-2 : When the activation energy of

forward reaction is less than that of backward reaction, then the increase in the rate of backward reaction is more than that of forward reaction on increasing the temperature.

(A) (A) (B) (B) (C) (C) (D) (D)

Sol.

17. Statement-1 : In a reversible endothermic reaction, E_{act} of forward reaction is higher than that of backward reaction

Statement-2 : The threshold energy of forward reaction is more than that of backward reaction

(A) (A) (B) (B) (C) (C) (D) (D)

Sol.

18. Statement-1 : A catalyst provides an alternative path to the reaction in which conversion of reactants into products takes place quickly

Statement-2 : The catalyst forms an activated complex of lower potential energy, with the reactants by which more number of molecules are able to cross the barrier per unit of time.

(A) (A) (B) (B) (C) (C) (D) (D)

Sol.

19. Statement-1 : Rate of a chemical reaction increases as the temperature is increased.

Statement-2 : As the temperature is increased fraction of molecules occupying E_r or more increases.

(A) (A) (B) (B) (C) (C) (D) (D)

Sol.

20. Statement-1 : For the bimolecular reaction to react, reactant must collide with each other.

Statement-2 : Bond breaking and formation occurs during the collision.

(A) (A) (B) (B) (C) (C) (D) (D)

Sol.

21. Statement-1 : Catalyst does not change the ΔH value of the reaction.

Statement-2 : Catalyst are generally added in very small quantities and not stoichiometrically.

(A) (A) (B) (B) (C) (C) (D) (D)

Sol.

22. Ozone decomposes according to the equation
 $2\text{O}_3(\text{g}) \rightarrow 3\text{O}_2(\text{g})$ Mechanism of the reaction is

Step I : $\text{O}_3(\text{g}) \rightleftharpoons \text{O}_2(\text{g}) + \text{O}(\text{g})$ (fast)

Step II : $\text{O}_3(\text{g}) + \text{O}(\text{g}) \longrightarrow 2\text{O}_2(\text{g})$ (slow)

Which of the following is correct ?

(A) for step I, molecularity is 2 (B) for step II, molecularity is 1

(C) step II is rate determining step

(D) Rate law expression for the overall reaction is

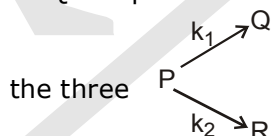
$$-\frac{d}{dt}[\text{O}_3] = k[\text{O}_3]^2[\text{O}_2]^{-1}$$

Sol.

23. Consider the following case of competing 1st order reactions

After the start of the reaction at $t = 0$, with only P, concentration

of Q is equal to R at all times. The time in which all



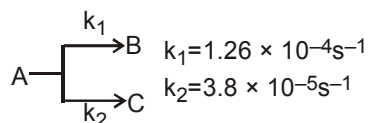
concentration will be equal is given by

(A) $t = \frac{2.303}{2k_1} \log_{10} 3$ (B) $t = \frac{2.303}{2k_2} \log_{10} 3$

(C) $t = \frac{2.303}{3k_1} \log_{10} 2$ (D) $t = \frac{2.303}{3k_2} \log_{10} 2$

Sol.

24. A substance undergoes first order decomposition. The decomposition follows two parallel first order reactions as



The % distribution of B and C is and respectively.

- (A) 76.83% B (B) 23.17% C
(C) 23.17% (D) 76.83% C

Sol.

25. Which of the following concepts are correct

- (A) If for, $A \rightarrow B$ $\Delta H = +q \text{ cal}$
then for, $B \rightarrow A$ $\Delta H = -q \text{ cal}$
(B) If for, $A \rightleftharpoons B$ equilibrium constant = K
then for, $B \rightleftharpoons A$ equilibrium constant = $\frac{1}{K}$
(C) If for, $A \rightarrow B$ rate constant = k
then for, $B \rightarrow A$ rate constant $\neq k$
(D) If for, $A \rightarrow B$ energy of activation = E
then for, $B \rightarrow A$ energy of activation = $-E$

Sol.

26. The basic theory behind Arrhenius equation is that

- (A) the activation energy and pre exponential factor are always temperature independent.
(B) the number of effective collisions is proportional to the number of molecules above a certain threshold energy.
(C) as the temperature increases, so does the number of molecules with energies exceeding threshold energy.
(D) rate constant is a function of temperature.

Sol.

27. Which of the following statements are correct about half life period ?

- (A) It is proportional to initial concentration for a zero order reaction.
(B) Average life = 1.44 times half life for a first order reaction.
(C) Time of 75% reaction is thrice of half life period in second order reaction.
(D) 99.9% reaction which is first order, takes place in 100 minutes if the rate constant of the reaction is 0.0693 min^{-1} .

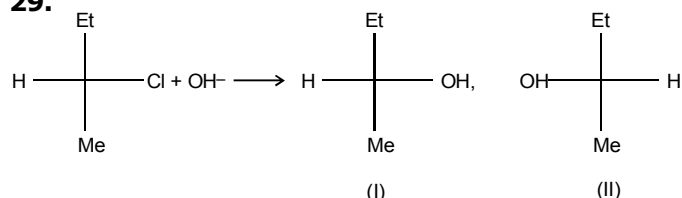
Sol.

28. For a reaction : $2A + 2B \rightarrow \text{products}$, the rate law expression is $r = k[A]^2[B]$. Which of the following is/are correct?

- (A) The reaction is first order w.r.t. B
(B) The reaction is of second order w.r.t. A
(C) The reaction is of third order, overall
(D) Slowest step of the reaction is given as $A + B \rightarrow AB$

Sol.

29.



Which of the following statements are correct ?

- (A) It is S_N1 if (I) or (II) is formed.
(B) It is S_N1 if equimolar mixture of (I) and (II) is formed.
(C) It is S_N2 if (I) or (II) is formed.
(D) It is S_N2 if (II) is formed.

Sol.**30.** Rate constant k varies with temperature byequation $\log_{10} k(\text{min}^{-1}) = 5 - \frac{2000}{T}$. We can conclude

- (A) pre exponential factor A is 10^5
 (B) E_a is 2000 k cal
 (C) E_a is 9.212 k cal
 (D) pre exponential factor A is 5

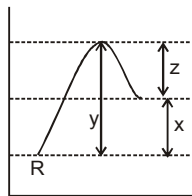
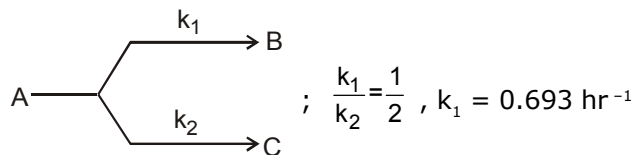
Sol.**31.** A reaction is catalysed by H^+ ion. In presence of HA, rate constant is $2 \times 10^{-3} \text{ min}^{-1}$ and in presence of HB rate constant is $1 \times 10^{-3} \text{ min}^{-1}$. HA and HB being strong acids, we may conclude that

- (A) HB is stronger acid than HA
 (B) HA is stronger acid than HB.
 (C) relative strength HA and HB is 2.
 (D) HA is weaker than HB and relative strength is 0.5.

Sol.**32.** The potential energy diagram for a reaction $\text{R} \rightarrow \text{P}$ is given below

Which of the following is true ?

- (A) E_a (forward) = y
 (B) E_a (backward) = z
 (C) $E_T = x + y$
 (D) $\Delta H_r = x$

Sol.**33.** An organic compound A decomposes by following two parallel first order mechanisms :

Select the correct statement(s)

- (A) If three moles of A are completely decomposed then 2 moles of B and 1 mole of C will be formed.
 (B) If three moles of A are completely decomposed then 1 moles of B and 2 mole of C will be formed.
 (C) half life for the decomposition of A is 20 min
 (D) half life for the decomposition of B is 0.33 min

Sol.**34.** Half life for which of the following varies with initial concentration $[A_0]$

- (A) zero order (B) first order
 (C) second order (D) third order

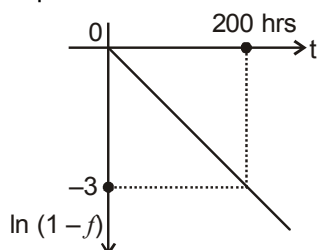
Sol.**35.** In which of the following, E_a for backward reaction is greater than E_a for forward reaction ?

- (A) $\text{a} \xrightarrow{E_a=50\text{kcal}} \text{b} \Delta H = -10\text{kcal}$
 (B) $\text{a} \xrightarrow{E_a=60\text{kcal}} \text{b} \Delta H = -20\text{kcal}$
 (C) $\text{a} \xrightarrow{E_a=50\text{kcal}} \text{b} \Delta H = +10\text{kcal}$
 (D) $\text{a} \xrightarrow{E_a=60\text{kcal}} \text{b} \Delta H = +20\text{kcal}$

Sol.**COMPREHENSION - 1**

Oxidation of metals is generally a slow electrochemical reaction involving many steps. These steps involve electron transfer reactions. A particular type of oxidation involve overall first order kinetics with re-

spect to fraction of unoxidised metal $(1 - f)$ surface thickness relative to maximum thickness (T) of oxidised surface, when metal surface is exposed to air for considerable period of time.



Rate law : $\frac{df}{dt} = k(1 - f)$, where $f = \frac{x}{T}$, x = thickness of oxide film at time 't' & T = thickness of oxide film at $t = \infty$. A graph of $\ln(1 - f)$ vs t is shown in the adjacent figure.

- 36.** The time taken for thickness to grow 50% of 'T' is
(A) 23.1 hrs (B) 46.2 hrs (C) 100 hrs (D) 92.4 hrs

Sol.

- 37.** The exponential variation of 'f' with t(hrs) is given by

- (A) $[1 - e^{-3t/200}]$ (B) $e^{-3t/200} - 1$
(C) $e^{-3t/200}$ (D) $e^{3t/200}$

Sol.

COMPREHENSION - 2



where $\frac{k_1}{k_2} = \frac{1}{2}$

Initially only 2 moles of A are present.

- 38.** The total number of moles of A, B & C at the end of 50% reaction are

- (A) 2 (B) 3 (C) 5 (D) None

Sol.

- 39.** Number of moles of B are

- (A) 2 (B) 1 (C) 0.666 (D) 0.333

Sol.

COMPREHENSION - 3

The rate of a reaction increases significantly with increase in temperature. Generally, rates of reaction are doubled for every 10° rise in temperature. Temperature coefficient gives us an idea about the change in rate of a reaction for every 10° change in temperature.

$$\text{Temperature coefficient } \mu = \frac{\text{Rate constant of } (T + 10)^\circ\text{C}}{\text{Rate constant at } T^\circ\text{C}}$$

Arrhenius gave an equation which describes rate constant k as a function of temperature is $k = A e^{-E_a/RT}$ where k is a rate constant

A is frequency factor or pre exponential factor

E_a is activation energy

T is temperature in kelvin and

R is universal gas constant

Equation when expressed in logarithmic form becomes

$$\log_{10} k = \log_{10} A - \frac{E_a}{2.303RT}$$

- 40.** For a reaction $E_a = 0$ and $k = 3.2 \times 10^5 \text{ s}^{-1}$ at 325 K . The value of k at 335 K would be

- (A) $3.2 \times 10^5 \text{ s}^{-1}$ (B) $6.4 \times 10^8 \text{ s}^{-1}$
(C) $12.8 \times 10^8 \text{ s}^{-1}$ (D) $25.6 \times 10^8 \text{ s}^{-1}$

Sol.

- 41.** For which of the following reactions k_{310}/k_{300} would be maximum ?

- (A) $P + Q \rightarrow R$; $E_a = 10 \text{ kJ}$ (B) $E + F \rightarrow D$; $E_a = 21 \text{ kJ}$
(C) $A + B \rightarrow C$; $E_a = 10.5 \text{ kJ}$ (D) $L + M \rightarrow N$; $E_a = 5 \text{ kJ}$

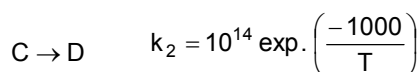
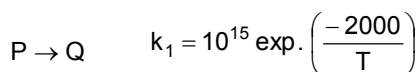
Sol.

42. Activation energies of two reaction are E_a and E'_a with $E_a > E'_a$. If the temperature of the reacting systems is increased from T_1 to T_2 (k' are rate constants at higher temperature).

- (A) $\frac{k'_1}{k_1} = \frac{k'_2}{k_2}$ (B) $\frac{k'_1}{k_1} < \frac{k'_2}{k_2}$
 (C) $\frac{k'_1}{k_1} > \frac{k'_2}{k_2}$ (D) $\frac{k'_1}{k_1} > \frac{2k'_2}{k_2}$

Sol.

43. For the reactions, following data is given



Temperature at which $k_1 = k_2$ is

- (A) 434.22 K (B) 1000 K (C) 2000 K (D) 868.44 K

Sol.

COMPREHENSION - 4

The rate and mechanism of chemical reactions are studied in chemical kinetics. The elementary reactions are single step reactions having no mechanism. The order of reaction and molecularity are same for elementary reactions. The rate of forward reaction $aA + bB \rightarrow cC + dD$ is given as :

$$\text{rate} = \left(\frac{dx}{dt} \right) = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt} \quad \text{or rate} =$$

$K[A]^a[B]^b$. In case of reversible reactions net rate expression can be written as : $\text{rate} = K_1[A]^a[B]^b - K_2[C]^c[D]^d$. At equilibrium, $\text{rate} = 0$. The constants K , K_1 , K_2 , are rate constants of respective reaction. In case of reactions governed by two or more steps reactions mechanism, the rate is given by the slowest step of mechanism.

44. The rate of formation of SO_3 in the following reaction : $2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3$ is 10 g sec^{-1} . The rate of disappearance of O_2 will be :

- (A) 5 g sec^{-1} (B) 100 g sec^{-1}
 (C) 20 g sec (D) 2 g sec^{-1}

Sol.

45. For the reaction : $aA \rightarrow bB$;

$$\log \left[\frac{-dA}{dt} \right] = \log \left[\frac{dB}{dt} \right] + 0.6, \text{ then } a : b \text{ is :}$$

- (A) 3.98 (B) 2.18 (C) 1.48 (D) 0

Sol.

46. For a reaction, $2\text{ND}_3 \rightarrow \text{N}_2 + 3\text{D}_2$;

$$\frac{-d[\text{ND}_3]}{dt} = K_1[\text{ND}_3] ; \quad \frac{d[\text{N}_2]}{dt} = K_2[\text{ND}_3] ;$$

$$\frac{d[\text{D}_2]}{dt} = K_3[\text{ND}_3], \text{ then :}$$

- (A) $K_1 = K_2 = K_3$ (B) $3K_1 = 6K_2 = 2K_3$
 (C) $K_1 = 2K_2 = K_3$ (D) $K_1 = K_2 = 2K_3$

Sol.

COMPREHENSION - 5

The rate of a reaction $\left(\frac{dx}{dt} \right)$ varies with nature, physical state and concentration of reactants, temperature, exposure to light and catalyst, whereas rate constant (K) varies with temperature and catalyst only. The rate constant K is given as $K = Ae^{-E_a/RT}$ where A is Arrhenius parameter or pre-exponential fac-

tor and E_a is energy of activation. The minimum energy required for a reaction is called threshold energy and the additional energy required by reactant molecules to attain threshold energy level is called energy of activation.

47. For a reaction, $A \rightarrow B$; if

$\log_{10} K(\text{sec}^{-1}) = 14 - \frac{1.25 \times 10^4}{T} \text{K}$, the Arrhenius parameter and energy of activation for the reaction are

- (A) 10^{14} sec^{-1} , 239.34 kJ (B) 14,57.6 kcal
(C) 10^{14} sec^{-1} , 23.93 kJ (D) 10^{14} sec , 5.76 kcal

Sol.

48. At what conditions exponential factor is 1 for a reaction :

- (A) Infinite temperature
(B) Free radical combination
(C) $E_a = 0$
(D) All of these

Sol.

49. For an endothermic reaction, which one is true if ΔH is heat of reaction and E_a is energy of activation :

- (A) $E_a > \Delta H$ (B) $E_a < \Delta H$
(C) $E_a \geq \Delta H$ (D) $E_a = 0$

Sol.

MATCH THE FOLLOWING

50. Match the column

Column - I

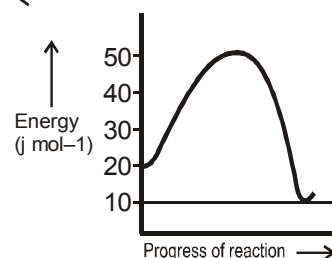
- (A) First order reaction
(B) Second order reaction
(C) Zero order reaction
(D) Fractional (+ve) order reaction

Column - II

- (P) Rate constant increases on increasing the concentration
(Q) Half life depends on the initial concentration
(R) Reaction must be complex
(S) Half life decreases on increasing the temperature
(T) The plot of concentration of reactant versus time will be a rectangular hyperbola

Sol.

51. Consider the following energy diagram for the reaction.



Column I

- (A) $E_a(f)$
(B) $E_a(b)$
(C) ΔH_r
(D) E_T

Column II

- (P) -10 kJ mol^{-1}
(Q) 40 kJ mol^{-1}
(R) 30 kJ mol^{-1}
(S) 50 kJ mol^{-1}

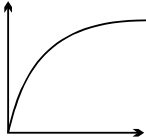
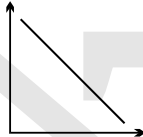
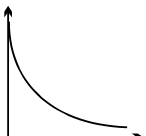
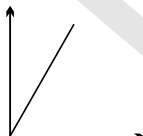
Sol.

52. For the reaction of type $A(g) \longrightarrow 2B(g)$ **Column-I** contains four entries and **column-II** contains four entries. Entry of column-I are to be matched with **ONLY ONE ENTRY** of column-II

Column I

- (A) $\frac{d[B]}{dt}$ vs $-\frac{d[A]}{dt}$ for first order
 (B) $[A]$ vs t for first order
 (C) $[B]$ vs t for first order
 (D) $[A]$ vs t for zero order

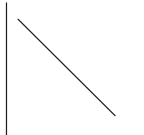
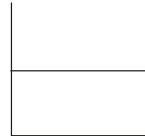
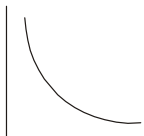
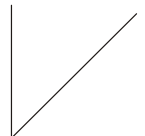
Column II

- (P)  (Q) 
 (R)  (S) 

Sol.

53. **Column-I** and **column-II**. Entry of column-I are to be matched with **ONE OR MORE THAN ONE ENTRIES** of column-II and vice versa.

Column I
(Graphs reaction $A \rightarrow$ Products)

- (A)  (B) 
 (C)  (D) 

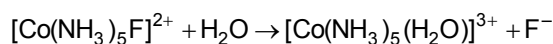
Column II
(Co-ordinates)

- (P) $\ln [A]$ (y-axis), t (x-axis) (order = 1)
 (Q) $t_{1/2}$ (y-axis), $[A_0]$ (x-axis) (order = 1)
 (R) r (y-axis), t (x-axis) (order > 0)
 (S) r (y-axis), t (x-axis) (order = 0)
 (T) $t_{1/2}$ (y-axis), $[A_0]$ (x-axis) (order > 1)
 (U) $\frac{1}{[A]}$ (y-axis), t (x-axis) (order = 2)
 (V) r (y-axis), $[A]$ (x-axis) (order = 1)

Sol.

INTEGER TYPE

54. The complex $[\text{Co}(\text{NH}_3)_5\text{F}]^{2+}$ reacts with water according to the equation.



The rate of the reaction = rate const. \times [complex]^a \times $[\text{H}^+]^b$. The reaction is acid catalysed i.e. $[\text{H}^+]$ does not change during the reaction. Thus rate = $k[\text{Complex}]^a$ where $k' = k [\text{H}^+]^b$, calculate 'a' and 'b' given the following data at 25°C.

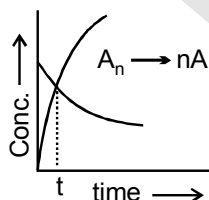
[Complex] M	$[\text{H}^+]$ M	$T_{1/2}$ hr	$T_{3/4}$ hr
0.1	0.01	1	2
0.2	0.02	0.5	1

Sol.

55. An optically active compound A upon acid catalysed hydrolysis yield two optically active compound B and C by pseudo first order kinetics. The observed rotation of the mixture after 20 min was 5° while after completion of the reaction it was -20° . If optical rotation per mole of A, B & C are 60° , 40° & -80° . Calculate half life of the reaction.

Sol.

56. Consider the following first order decomposition process:



Here, "t" corresponds to the time at which $\left(\frac{1}{6}\right)^{\text{th}}$ of reactant is decomposed. The value of "n" is

Sol.

57. For a 1st order reaction (gaseous) (cont. V, T)
 $aA \rightarrow (b-1)B + C$ (with $b > a$) the pressure of the system increased by $50\left(\frac{b}{a}-1\right)\%$ in a time of 10 min. The half life of the reaction is therefore (in min.).

Sol.

58. The rate of decomposition of $\text{NH}_3(\text{g})$ at 10 atm on platinum surface is zero order. What is rate of formation (in M min^{-1}) of $\text{H}_2(\text{g})$, if rate constant of reaction $2\text{NH}_{3(\text{g})} \rightarrow \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$ is 2.0 M min^{-1} ?

Sol.

59. $5A \rightarrow \text{Product}$

In above reaction, half-life period is directly proportional to initial concentration of reactant. The initial rate of reaction is $400 \text{ mol lit}^{-1} \text{ min}^{-1}$.

Calculate the half-life period (in sec) when initial concentration of reactant is 200 mol lit^{-1} .

Sol.

60. In an elementary reaction $A(g) + 2B(g) \longrightarrow C(g)$ the initial pressure of A and B are $P_A = 0.40 \text{ atm}$ and $P_B = 0.60 \text{ atm}$ respectively. After time T , if pressure of C is observed 0.1 atm , then find the value of

$$\frac{r_i(\text{initial rate of reaction})}{r_t(\text{rate of reaction after time } t)}$$

Sol.

61. Carbon monoxide reacts with O_2 to form CO_2 : $2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$ information on this reaction is given in the table below.

[CO] mol/L	[O ₂] mol/L	Rate of reaction (mol/L.min)
0.02	0.02	4×10^{-5}
0.04	0.02	1.6×10^{-4}
0.02	0.04	8×10^{-5}

What is the value for the rate constant for the reaction in proper related unit ?

Sol.

62. Half-life for the zero order reaction, $A(g) \rightarrow B(g) + C(g)$ and half-life for the first order reaction $X(g) \rightarrow Y(g) + Z(g)$ is equal. If completion time for the zero order reaction is 13.86 min , then calculate the rate constant (in hr^{-1}) for the reaction $X(g) \rightarrow Y(g) + Z(g)$.

Sol.

63. For any acid catalysed reaction, $A \xrightarrow{H^+} B$

Half-life period is independent of concentration of A at given pH. At same concentration of A half-life time is 10 min at $\text{pH}=2$ and half-life time is 100 min at $\text{pH}=3$. If the rate law expression of reaction is $r = k[A]^x[H^+]^y$ then calculate the value of $(x+y)$.

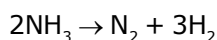
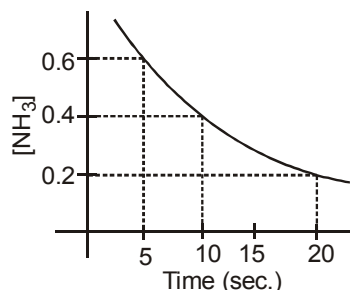
Sol.

64. For a reaction, $A \rightleftharpoons B$ equilibrium constant is 1.66 and $k_{\text{forward}} = 0.166 \text{ hr}^{-1}$.

Calculate the time (in hours) when concentration of B is 80% of its equilibrium concentration.

(Given : $\ln 25 = 3.20$)

Sol.

EXERCISE – III**SUBJECTIVE PROBLEMS (JEE ADVANCED)****Q.1** For the reactiona curve is plotted between $[\text{NH}_3]$ is time as shown

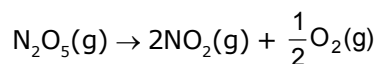
Calculate

- (a) rate of disappearance between 5 to 10 sec
 (b) rate of disappearance between 10 to 20 sec

Sol.

Q.2 For the reaction $3\text{BrO}^- \rightarrow \text{BrO}_3^- + 2\text{Br}^-$ in an alkaline aqueous solution, the value of the second order (in BrO^-) rate constant at 80°C in the rate law for $-\frac{\Delta[\text{BrO}^-]}{\Delta t}$ was found to be $0.056 \text{ L mol}^{-1}\text{s}^{-1}$. What is the rate of constant when the rate law is written for

- (a) $\frac{\Delta[\text{BrO}_3^-]}{\Delta t}$, (b) $\frac{\Delta[\text{Br}^-]}{\Delta t}$?

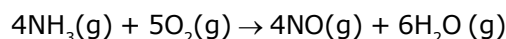
Sol.**Q.3** Dinitropentaoxide decomposes as follows :Given that $-\frac{d[\text{N}_2\text{O}_5]}{dt} = k_1[\text{N}_2\text{O}_5]$

$$\frac{d[\text{NO}_2]}{dt} = k_2[\text{N}_2\text{O}_5]$$

$$\frac{d[\text{O}_2]}{dt} = k_3[\text{N}_2\text{O}_5]$$

What is the relation between k_1 , k_2 and k_3 ?**Sol.****Q.4** The reaction $2\text{A} + \text{B} + \text{C} \rightarrow \text{D} + \text{E}$ is found to be first order in A second order in B and zero order in C.

- (i) Give the rate law for the reaction in the form of differential equation.
 (ii) What is the effect in rate of increasing concentrations of A, B, and C two times ?

Sol.**Q.5** For the elementary reaction $2\text{A} + \text{B}_2 \rightarrow 2\text{AB}$. Calculate how much the rate of reaction will change if the volume of the vessel is reduced to one third of its original volume?**Sol.****Q.6** Ammonia and oxygen reacts at higher temperatures asIn an experiment, the concentration of NO increases by $1.08 \times 10^{-2} \text{ mol litre}^{-1}$ in 3 seconds. Calculate.

- (i) rate of reaction.
 (ii) rate of disappearance of ammonia
 (iii) rate of formation of water.

Sol.

Q.7 In the following reaction $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$
rate of formation of O_2 is 3.6 M min^{-1} .

(a) What is rate of formation of H_2O ?

(b) What is rate of disappearance of H_2O_2 ?

Sol.

Q.8 The reaction $\text{A(g)} + 2\text{B(g)} \rightarrow \text{C(g)} + \text{D(g)}$ is an elementary process. In an experiment, the initial partial pressure of A & B are $P_A = 0.6$ and $P_B = 0.8 \text{ atm}$, if $P_C = 0.2 \text{ atm}$ then calculate the ratio of rate of reaction relative to initial rate.

Sol.**ZERO ORDER**

Q.9 In the following reaction, rate constant is $1.2 \times 10^{-2} \text{ Ms}^{-1}$ $\text{A} \rightarrow \text{B}$. What is concentration of B after 10 and 20 min., if we start with 10 M of A.

Sol.

Q.10 For the following data for the reaction $\text{A} \rightarrow \text{products}$. Calculate the value of k .

Time (min.)	[A]
0.0	0.10 M
1.0	0.09 M
2.0	0.08 M

Sol.

Q.11 The rate constant for a zero order reaction is $2 \times 10^{-2} \text{ mol L}^{-1} \text{ sec}^{-1}$, if the concentration of the reactant after 25 sec is 0.25 M, calculate the initial concentration.

Sol.

Q.12 A drop of solution (volume 0.10 ml) contains 6×10^{-6} mole of H^+ , if the rate constant of disappearance of H^+ is $1 \times 10^7 \text{ mole litre}^{-1} \text{ sec}^{-1}$. How long would it take for H^+ in drop to disappear ?

Sol.

Q.13 A certain substance A is mixed with an equimolar quantity of substance B. At the end of an hour A is 75% reacted. Calculate the time when A is 10% unreacted. (Given : order of reaction is zero)

Sol.**FIRST ORDER**

Q.14 A first order reaction is 75% completed in 72 min. How long time will it take for

(i) 50% completion (ii) 87.5% completion

Sol.

Q.15 A first order reaction is 20% complete in 10 min. Calculate (i) the specific rate constant, (ii) the time taken for the reactions to go to 75% completion.

Sol.

Q.16 Show that in case of unimolecular reaction, the time required for 99.9% of the reaction to take place is ten times that required for half of the reaction.

Sol.

Q.17 A first order reaction has a rate constant is $1.5 \times 10^{-3} \text{ sec}^{-1}$. How long will 5.0 g of this reactant take to reduce to 1.25 g.

Sol.

Q.18 A drug is known to be ineffective after it has decomposed 30%. The original concentration of a sample was 500 units/ml. When analyzed 20 months later, the concentration was found to be 420 units/ml. Assuming that decomposition is of I order, what will be the expiry time of the drug?

Sol.

Q.19 A viral preparation was inactivated in a chemical bath. The inactivation process was found to be first order in virus concentration. At the beginning of the experiment 2.0% of the virus was found to be inactivated per minute. Evaluate k for inactivation process.

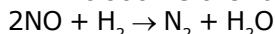
Sol.

Q.20 Consider the reaction : $A \rightarrow B + C$. Initial concentration of A is 1 M. 20 minutes time is required for completion of 20% reaction. If $\frac{d[B]}{dt} = k[A]$, then calculate half life ($t_{1/2}$) of reaction.

Sol.

Q.21 The reaction $\text{SO}_2\text{Cl}_2(\text{g}) \rightarrow \text{SO}_2(\text{g}) + \text{Cl}_2(\text{g})$ is a first order gas reaction with $k = 2.2 \times 10^{-5} \text{ sec}^{-1}$ at 320°C . What % of SO_2Cl_2 is decomposed on heating this gas for 90 min.

Sol.

ORDER OF REACTION & RATE LAW**Q.22** At 800° C the rate of reactionChanges with the concentration of NO and H₂ are

[NO] in M	[H ₂] in M	$-\frac{1}{2} \frac{d[\text{NO}]}{dt}$ in M sec ⁻¹
-----------	------------------------	---

(i) 1.5×10^{-4} 4×10^{-3} 4.4×10^{-4} (ii) 1.5×10^{-4} 2×10^{-3} 2.2×10^{-4} (iii) 3.0×10^{-4} 2×10^{-3} 8.8×10^{-4}

(a) What is the order of this reaction ?

(b) What is the rate equation for the reaction ?

(c) What is the rate when

[H₂] = 1.5×10^{-3} M and [NO] = 1.1×10^{-3} M ?**Sol.****Q.23** The data below are for the reaction if NO and Cl₂ to form NOCl at 295 K

Concentration of Cl ₂ [M]	Concentration of NO	Initial Rate (Ms ⁻¹)
0.05	0.05	1×10^{-3}
0.15	0.05	3×10^{-3}
0.05	0.15	9×10^{-3}

(a) What is the order w.r.t NO and Cl₂ in the reaction.

(b) Write the rate expression

(c) Calculate the rate constant

(d) Determine the reaction rate when concentration of Cl₂ and NO are 0.2 M & 0.4 M respectively.**Sol.****Q.24** The catalytic decomposition of N₂O by gold at 900° C and at an initial pressure of 200mm is 50% complete in 53 minutes and 73% complete in 100 minutes.

(i) What is the order of the reaction ?

(ii) Calculate the velocity constant.

(iii) How much of N₂O will decompose in 100 min. at the same temperature but at initial pressure of 600 mm?**Sol.****Q.25** The following data are for the reaction A + B → products :

Conc. A (M)	Conc. B (M)	Initial Rate (mol L ⁻¹ s ⁻¹)
0.1	0.1	4.0×10^{-4}
0.2	0.2	1.6×10^{-3}
0.5	0.1	2.0×10^{-3}
0.5	0.5	1.0×10^{-2}

(i) What is the order with respect to A and B for the reaction ?

(ii) Calculate the rate constant.

(iii) Determine the reaction rate when the concentrations of A and B are 0.2 M and 0.35M, respectively.

Sol.**Q.26** The pressure of a gas decomposing at the surface of a solid catalyst has been measured different times and the results are given below

t (sec)	0	100	200	300
Pr. (Pascal)	4×10^3	3.5×10^3	3×10^3	2.5×10^3

Determine the order of reaction, its rate constant.

Sol.

Q.27 The half life period of decomposition of a compound is 50 minutes. If the initial concentration is halved, the half life period is reduced to 25 minutes. What is the order of reaction ?

Sol.

Q.28 At 600°C, acetone (CH_3COCH_3) decomposes to ketene ($\text{CH}_2 = \text{C} = \text{O}$) and various hydrocarbons. Given the initial rate data in the table :

- What is the order ?
- Write rate law
- Calculate rate constant
- Calculate the rate of decomposition when the acetone concentration is $1.8 \times 10^{-3} \text{ M}$

	Experiment	Initial $[\text{CH}_3\text{COCH}_3]$	Rate M s^{-1}
1.		$6.0 \times 10^{-3} \text{ M}$	5.2×10^{-5}
2.		$9.0 \times 10^{-3} \text{ M}$	7.8×10^{-5}
3.		$1.8 \times 10^{-3} \text{ M}$?

Sol.

HALF LIFE

Q.29 The half life period of a first order reaction is 50 min. In what time will it go to 90% completion ?

Sol.

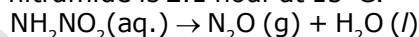
Q.30 A first order reaction has $k = 1.5 \times 10^{-6}$ per second at 200°C. If the reaction is allowed to run for 10 hrs., what percentage of the initial concentration would have changed into the product ? What is the half life of this reaction ?

Sol.

Q.31 Show that in case of a first order reaction, the time required for 93.75% of the reaction to take place is four times that required for half of the reaction.

Sol.

Q.32 The half time of the first order decomposition of nitramide is 2.1 hour at 15°C.



If 6.2 g of NH_2NO_2 is allowed to decompose, calculate (i) time taken for NH_2NO_2 to decompose 99%, and (ii) volume of dry N_2O produced at this point, measured at 1 atm & 273 K.

Sol.

Q.33 A flask contains a mixture of compounds A and B. Both compounds decompose by first-order kinetics. The half-lives are 54.0 min for A and 18.0 min. for B. If the concentrations of A and B are equal initially, how long will it take for the concentration of A to be four times that of B ?

Sol.

Q.34 Two substances A ($t_{1/2} = 5$ mins) and B ($t_{1/2} = 15$ mins) follow first order kinetics are taken in such a way that initially $[\text{A}] = 4[\text{B}]$. Calculate the time after which the concentration of both the substance will be equal.

Sol.

CONCENTRATION REPLACED BY OTHER QUANTITIES IN FIRST ORDER INTEGRATED RATE LAW**Q.35** In this case we have

	A	→	B	+	C
Time			t		∞
Total pressure of A + B + C			P ₂		P ₃

Find k.

Sol.**Q.36** $A \rightarrow B + C$

Time		t	∞
Total pressure of (B + C)		P ₂	P ₃

Find k.

Sol.**Q.37** $A \rightarrow B + C$

Time	0	t
Volume of reagent	V ₁	V ₂

The reagent reacts with A, B and C. Find k.

Sol.**Q.38** $A \rightarrow 2B + 3C$

Time	t	∞
Volume of reagent	V ₂	V ₃

Reagent reacts with all A, B and C. Find K.

Sol.**Q.39** $S \rightarrow G + F$

Time	t	∞
Rotation of Glucose & Fructose	r _t	r _∞

Find k.

Sol.**Q.40** At 27°C it was observed during a reaction of hydrogenation that the pressure of hydrogen gas decreases from 2 atmosphere to 1.1 atmosphere in 75 minutes. Calculate the rate of reaction (in M sec⁻¹) and rate of reaction in terms of pressure.**Sol.****Q.41** At 100° C the gaseous reaction $A \rightarrow 2B + C$ was observed to be of first order. On starting with pure A it is found that at the end of 10 minutes the total pressure of system is 176 mm. Hg and after a long time 270 mm Hg. From these data find (a) initial pressure of A (b) the pressure of A at the end of 10 minutes (c) the specific rate of reaction and (d) the half life period of the reaction ?**Sol.**

Q.42 The reaction $\text{AsH}_3(\text{g}) \rightarrow \text{As}(\text{s}) + \frac{3}{2}\text{H}_2(\text{g})$ was followed at constant volume at 310°C by measuring the gas pressure at intervals. Show from the following figures that reaction is of first order.

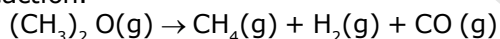
Time (in hrs)	0	5	7.5	10
Total pressure (in mm)	758	827	856	882

Sol.

Q.43 The decomposition of N_2O_5 according to the equation $2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$ is a first order reaction. After 30 min. from start of decomposition in a closed vessel the total pressure developed is found to be 284.5 mm Hg. On complete decomposition, the total pressure is 584.5 mm Hg. Calculate the rate constant of the reaction.

Sol.

Q.44 The thermal decomposition of dimethyl ether as measured by finding the increase in pressure of the reaction.



At 500°C is as follows :

Time (sec.)	390	1195	3155	∞
Pre. increase (mm Hg)	96	250	467	619

the initial pressure of ether was 312 mm Hg. Write the rate equation for this reaction and determine the rate constant of reaction.

Sol.

Q.45 From the following data show that decomposition of H_2O_2 in aqueous solution is first order.

Time (in minutes)	0	10	20
Volume (in c.c. of KMnO_4)	22.8	13.3	8.25

Sol.

Q.46 A definite volume of H_2O_2 under going spontaneous decomposition required 22.8 cc. of standard permanganate solution for titration. After 10 and 20 minutes respectively the volumes of permanganate required were 13.8 and 8.25 c.c.

(a) Find order of reaction. How many the result be explained ?

(b) Calculate the time required for the decomposition to be half completed.

(c) Calculate the fraction of H_2O_2 decomposed after 25 minutes.

Sol.

Q.47 The following data were obtained in experiment on inversion of cane sugar.

Time (minutes)	0	60	120	180	360	∞
Angle of rotation (degree)		+13.1	+11.6	+10.2	+9.0	+5.87

rotation (degree)

Show that the reaction is of first order. After what time would you expect a zero reading in polarimeter ?

Sol.

Q.48 In the hydrolysis of propyl acetate in the presence of dilute hydrochloric acid in dilute aqueous solution the following data were recorded :

Time from start in minutes 60 350

Percentage of ester decomposed 18.17 69.12

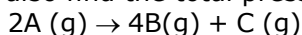
Calculate the time in which half the ester was decomposed.

Sol.

Q.49 Hydrogen peroxide solution was stored in a mild steel vessel. It was found, however, that the hydrogen peroxide decomposed on the walls of the vessel (a first order reaction). An experiment with 100 ml of a solution gave 10.31 ml oxygen (corrected to 1 atm & 273 K) after 5.1 days under similar storage conditions. Find how long the peroxide can be stored before the loss of 20.00 ml oxygen occurs (per 100 ml solution) if complete decomposition of the sample to H_2O_2 gave 46.34 ml oxygen.

Sol.

Q.50 The reaction given below, rate constant for disappearance of A is $7.48 \times 10^{-3} \text{ sec}^{-1}$. Calculate the time required for the total pressure in a system containing A at an initial pressure of 0.1 atm to rise to 0.145 atm and also find the total pressure after 100 sec.



Sol.

PARALLEL AND SEQUENTIAL REACTION

Q.51 For a reaction $\text{X} \xrightarrow{k_1} \text{Y}$, $\text{X} \xrightarrow{k_2} \text{Z}$, calculate value of ratio, $\frac{[\text{X}]_t}{[\text{Y}] + [\text{Z}]}$ at any given instant t.

Sol.

Q.52 $\text{A} \xrightarrow{k_1} \text{B}$, $\text{A} \xrightarrow{k_2} \text{C}$ $k_1 = x \text{ hr}^{-1}$; $k_1 : k_2 = 1 : 10$. Calculate $\frac{[\text{C}]}{[\text{A}]}$ after one hour from the start of the reaction.

Assuming only A was present in the beginning.

Sol.

Q.53 A substance undergoes first order decomposition. The decomposition follows two parallel first order reactions as

$\text{A} \xrightarrow{k_1} \text{B}$, $\text{A} \xrightarrow{k_2} \text{C}$; $k_1 = 1.26 \times 10^{-4} \text{ sec}^{-1}$ and $k_2 = 3.6 \times 10^{-5} \text{ sec}^{-1}$. Calculate the % distribution of B & C.

Sol.

Q.54 For a reaction $\text{A} \rightarrow \text{B} \rightarrow \text{C}$ $t_{1/2}$ for A & B are 4 and 2 minutes respectively. How much time would be required for the B to reach maximum concentration.

Sol.

TEMPERATURE DEPENDENCE OF RATE

Q.55 For the two parallel reactions $A \xrightarrow{k_1} B$ and $A \xrightarrow{k_2} C$, show that the activation energy E' for the disappearance of A is given in terms of activation energies E_1 and E_2 for the two paths by

$$E' = \frac{k_1 E_1 + k_2 E_2}{k_1 + k_2}$$

Sol.

(ACTIVATION ENERGY)

Q.56 The energy of activation of a first order reaction is $104.5 \text{ kJ mole}^{-1}$ and pre-exponential factor (A) is $5 \times 10^{-13} \text{ sec}^{-1}$. At what temperature, will the reaction have a half life of 1 minute ?

Sol.

Q.57 The specific rate constant for a reaction increases by a factor of 4, if the temperature is changed from 27°C to 47°C . Find the activation energy for the reaction.

Sol.

Q.58 The energy of activation and specific rate constant for a first order reaction at 25°C are 100 kJ/mole and $3.46 \times 10^{-5} \text{ sec}^{-1}$ respectively. Determine the temperature at which half life of the reaction is 2 hours.

Sol.

Q.59 A first order reaction is 50% complete in 30 minutes at 27°C and in 10 minutes at 47°C . Calculate the

(a) rate constant for the reaction at 27°C & 47°C and
(b) energy of activation for the reaction.

Sol.

Q.60 A catalyst lowers the activation energy for a certain reaction from 75 kJ to 25 kJ mol^{-1} . What will be the effect on the rate of reaction at 25°C , after things being equal.

Sol.

Q.61 Given that the temperature coefficient for the saponification of ethyl acetate by NaOH is 1.75. Calculate activation energy for the saponification of ethyl acetate.

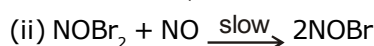
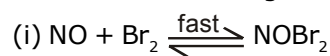
Sol.

Q.62 The rate constants of a reaction at 500 K and 700 K are 0.02 s^{-1} and 0.07 s^{-1} , respectively. Calculate the values of E_a and A at 500 K .

Sol.

MECHANISM OF REACTION

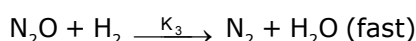
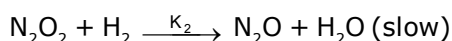
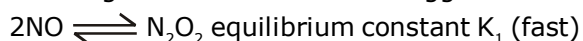
Q.63 The reaction $2\text{NO} + \text{Br}_2 \rightarrow 2\text{NOBr}$, is supposed to follow the following mechanism



Suggest the rate of law expression.

Sol.

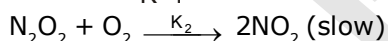
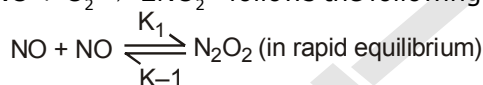
Q.64 For the reaction $2\text{H}_2 + 2\text{NO} \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$, the following mechanism has been suggested :



Establish the rate law for given reaction.

Sol.

Q.65 Reaction between NO and O_2 to form NO_2 is $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ follows the following mechanism



Show that the rate of reaction is given by

$$\frac{1}{2} \left(\frac{d[\text{NO}_2]}{dt} \right) = K[\text{NO}]^2[\text{O}_2]$$

Sol.

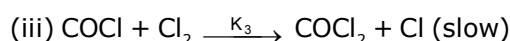
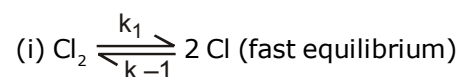
66. For the mechanism $\text{A} + \text{B} \xrightleftharpoons[k_2]{k_1} \text{C}; \text{C} \xrightarrow{k_3} \text{D}$

(a) Derive the rate law using the steady-state approximation to eliminate the concentration of C.

(b) Assuming that $k_3 \ll k_2$, express the pre-exponential factor A and E_a for the apparent second-order rate constant in terms of A_1 , A_2 and A_3 and E_{a1} , E_{a2} and E_{a3} for the three steps.

Sol.

67. The reaction of formation of phosgene from CO and Cl_2 is $\text{CO} + \text{Cl}_2 \rightarrow \text{COCl}_2$. The proposed mechanism is



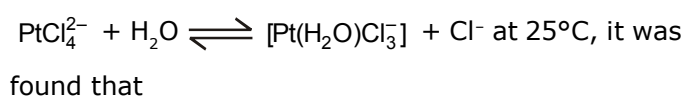
Show that the above mechanism leads to the following rate law

$$\frac{d[\text{COCl}_2]}{dt} = K[\text{CO}][\text{Cl}_2]^{3/2} \quad \text{Where}$$

$$K = k_3 \cdot \frac{k_2}{k-2} \left(\frac{k_1}{k-1} \right)^{1/2}$$

Sol.

68. The approach to the following equilibrium was observed kinetically from both directions :



$$-\frac{\Delta}{\Delta t} [\text{PtCl}_4^{2-}] = [3.9 \times 10^{-5} \text{ sec}^{-1}] [\text{PtCl}_4^{2-}] - [2.1 \times 10^{-3} \text{ L.mol}^{-1} \text{ sec}^{-1}] \times [\text{Pt}(\text{H}_2\text{O})\text{Cl}_3]^- [\text{Cl}^-]$$

What is the value of equilibrium constant for the complexation of the fourth Cl^- by Pt(II) ?

Sol.

69. A solution of A is mixed with an equal volume of a solution of B containing the same number of moles, and the reaction $A + B = C$ occurs. At the end of 1h, A is 75% reacted. How much of A will be left unreacted at the end of 2 h if the reaction is (a) first order in A and zero order in B; (b) first order in both A and B ; and (c) zero order in both A and B ?

Sol.

70. The decomposition of a compound P, at temperature T according to the equation

$2P_{(g)} \rightarrow 4Q_{(g)} + R_{(g)} + S_{(l)}$ is the first order reaction. After 30 minutes from the start of decomposition in a closed vessel, the total pressure developed is found to be 317 mm Hg and after a long period of time the total pressure observed to be 617 mm Hg. Calculate the total pressure of the vessel after 75 minutes, if volume of liquid S is supposed to be negligible. Also calculate the time fraction $t_{7/8}$.

Given : Vapour pressure of $S(l)$ at temperature $T = 32.5$ mm Hg

Sol.

71. A certain reactant B^{n+} is getting converted to $B^{(n+4)+}$ in solution. The rate constant of this reaction is measured by titrating a volume of the solution with a reducing reagent which only reacts with B^{n+} and $B^{(n+4)+}$. In this process, it converts B^{n+} to $B^{(n-2)+}$ and $B^{(n+4)+}$ to $B^{(n-1)+}$. At $t = 0$, the volume of the reagent consumed is 25 ml and at $t = 10$ min, the volume used up is 32 ml. Calculate the rate constant of the conversion of B^{n+} to $B^{(n+4)+}$ assuming it to be a first order reaction.

Sol.

72. A metal slowly forms an oxide film which completely protects the metal when the film thickness is 3.956 thousandths of an inch. If the film thickness is 1.281 thou. in 6 weeks, how much longer will it be before it is 2.481 thou? The rate of film formation follows first order kinetics.

Sol.

73. A vessel contains dimethyl ether at a pressure of 0.4 atm. Dimethyl ether decomposes as $\text{CH}_3\text{OCH}_3(\text{g}) \rightarrow \text{CH}_4(\text{g}) + \text{CO}(\text{g}) + \text{H}_2(\text{g})$. The rate constant of decomposition is $4.78 \times 10^{-3} \text{ min}^{-1}$. Calculate the ratio of initial rate of diffusion to rate of diffusion after 4.5 hours of initiation of decomposition. Assume the composition of gas present and composition of gas diffusing to be same.

Sol.

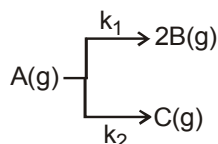
75. The gaseous reaction : $n_1\text{A}(\text{g}) \rightarrow n_2\text{B}(\text{g})$ is first order with respect to A. It is studied at a constant pressure, with a_0 as the initial amount of A. Show that the volume of system at the concentration of A at time 't' are given by the expressions.

$$V = V_0 \left[\left(\frac{n_2}{n_1} \right) - \left(\frac{n_2}{n_1} - 1 \right) \exp(-n_1 kt) \right] ;$$

$$[\text{A}]_t = [\text{A}]_0 \left[\frac{\exp(-n_1 kt)}{\left(\frac{n_2}{n_1} \right) - \left\{ \left(\frac{n_2}{n_1} \right) - 1 \right\} \exp(-n_1 kt)} \right]$$

Sol.

74. For the following first order gaseous reaction



The initial pressure in a container of capacity V litres is 1 atm. Pressure at time $t = 10 \text{ sec}$ is 1.4 atm and after infinite time it becomes 1.5 atmosphere. Find the rate constant k_1 and k_2 for the appropriate reactions.

Sol.

EXERCISE – IV**PREVIOUS YEARS****LEVEL – I****JEE MAIN**

Q.1 For the reaction $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$ the true relationship is - **[AIEEE-2002]**

- (A) $-\frac{d[\text{H}_2]}{dt} = \frac{d[\text{I}_2]}{dt} = \frac{d[\text{HI}]}{dt}$
 (B) $\frac{d[\text{H}_2]}{dt} = -\frac{d[\text{I}_2]}{dt} = \frac{1}{2} \frac{d[\text{HI}]}{dt}$
 (C) $-\frac{2d[\text{H}_2]}{dt} = -\frac{2d[\text{I}_2]}{dt} = \frac{d[\text{HI}]}{dt}$
 (D) $\frac{2d[\text{H}_2]}{dt} = -\frac{2d[\text{I}_2]}{dt} = \frac{1}{2} \frac{d[\text{HI}]}{dt}$

Sol.

Sol.

Q.2 A chemical reaction $[2\text{A}] + [2\text{B}] + [\text{C}] \longrightarrow$ product follows the rate equation : $r \propto [\text{A}] [\text{B}]^2$ then order of reaction is - **[AIEEE-2002]**

- (A) 0 (B) 1 (C) 2 (D) 3

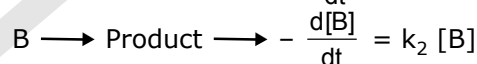
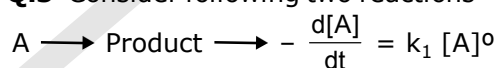
Sol.

Q.4 In the equation $Kt = \log C_0 - \log C_t$, the curve between t and $\log C_t$ is - **[AIEEE-2002]**

- (A) a straight line (B) a parabola
(C) a hyperbola (D) none

Sol.

Q.5 Consider following two reactions



Units of k_1 and k_2 are expressed in terms of molarity (mol L^{-1}) and time (sec^{-1}) as - **[AIEEE-2002]**

- (A) sec^{-1} , M sec^{-1} (B) M sec^{-1} , M sec^{-1}
(C) sec^{-1} , $\text{M}^{-1} \text{sec}^{-1}$ (D) M sec^{-1} , sec^{-1}

Sol.

Q.3 The unit of rate constant of first & second order reaction is respectively - **[AIEEE-2002]**

- (A) time^{-1} , $\text{mole}^{-1} \cdot \text{litre} \cdot \text{time}^{-1}$
 (B) mole ltr^{-1} , time^{-1}
 (C) $\text{mole}^{-1} \cdot \text{litre} \cdot \text{time}^{-1}$, time^{-1}
 (D) sec^{-1} , litre^{-1}

Q.6 H_2 gas is adsorbed on the metal surface like tungsten. This follows..... order reaction –

[AIEEE-2002]

- (A) Third (B) Second
(C) Zero (D) First

Sol.

Q.7 In respect of the equation $k = Ae^{-E_a/RT}$ in chemical kinetics, which one of the following statement is correct?

[AIEEE-2003]

- (A) E_a is energy of activation
(B) R is Rydberg's constant
(C) k is equilibrium constant
(D) A is adsorption factor

Sol.

Sol.

Q.9 The rate law for a reaction between substances A and B is given by

Rate = $k[A]^n[B]^m$ On doubling the concentration of A and halving the concentration of B, the ratio of the new rate to the earlier rate of the reaction will be as–

[AIEEE-2003]

- (A) $(n-m)$ (B) $2^{(n-m)}$ (C) $\frac{1}{2^{(m+n)}}$ (D) $(m+n)$

Sol.

Q.10 In a first order reaction, the concentration of the reactant, decreases from 0.8 M to 0.4 M in 15 minutes. The time taken for the concentration to change from 0.1 M to 0.025 M is –

[AIEEE-2004]

- (A) 30 minutes (B) 15 minutes
(C) 7.5 minutes (D) 60 minutes

Sol.

Q.8 For the reaction system: $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2\text{NO}_2(\text{g})$ volume is suddenly reduced to half its value by increasing the pressure on it. If the reaction is of first order with respect to O_2 and second order with respect to NO, the rate of reaction will –

[AIEEE-2003]

- (A) Increase to eight times of its initial value
(B) Increase to four times of its initial value
(C) Decrease to one-fourth of its initial value
(D) Decrease to one-eighth of its initial value

Q.11 The rate equation for the reaction $2A + B \rightarrow C$ is found to be : rate = $k[A][B]$. The correct statement in relation to this reaction is that the

[AIEEE-2004]

- (A) unit of k must be s^{-1}
- (B) $t_{1/2}$ is a constant
- (C) rate of formation of C is twice the rate of disappearance of A
- (D) value of k is independent of the initial concentrations of A and B

Sol.

Sol.

Q.12 Consider an endothermic reaction $X \rightarrow Y$ with the activation energies E_b and E_f for the backward and forward reactions, respectively. In general

[AIEEE-2005]

- (A) $E_b > E_f$
- (B) $E_b < E_f$
- (C) there is no definite relation between E_b and E_f
- (D) $E_b = E_f$

Sol.

Q.14 $t_{1/4}$ can be taken as the time taken for the concentration of a reactant to drop to $\frac{3}{4}$ of its initial value. If the rate constant for a first order reaction is K , $t_{1/4}$ can be written as –

[AIEEE-2005]

- (A) $0.29/K$
- (B) $0.10/K$
- (C) $0.75/K$
- (D) $0.69/K$

Sol.

Q.15 A reaction was found to be second order with respect to the concentration of carbon monoxide. If the concentration of carbon monoxide is doubled, with everything else kept the same, the rate of reaction will –

[AIEEE 2006]

- (A) triple
- (B) increase by a factor of 4
- (C) double
- (D) remain unchanged

Sol.

Q.13 A reaction involving two different reactants can never be –

[AIEEE-2005]

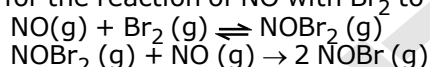
- (A) first order reaction
- (B) unimolecular reaction
- (C) bimolecular reaction
- (D) second order reaction

Q.16 Rate of reaction can be expressed by Arrhenius equation as $k = Ae^{-E/RT}$, In this equation, E represents
[AIEEE 2006]

- (A) the energy below which colliding molecules will not react
(B) the total energy of the reacting molecule at a temperature, T
(C) the fraction of molecules with energy greater than the activation energy of the reaction
(D) the energy above which all the colliding molecules will react

Sol.

Q.17 The following mechanism has been proposed for the reaction of NO with Br₂ to form NOBr :



If the second step is the rate determining step, the order of the reaction with respect to NO (g) is -

[AIEEE 2006]

- (A) 0 (B) 3 (C) 2 (D) 1

Sol.

Q.18 The energies of activation for forward and reverse reactions for $\text{A}_2 + \text{B}_2 \rightleftharpoons 2\text{AB}$ are 180 kJ mol⁻¹ and 200 kJ mol⁻¹ respectively. The presence of a catalyst lowers the activation energy of both (forward and reverse) reactions by 100 kJ mol⁻¹. The enthalpy change of the reaction ($\text{A}_2 + \text{B}_2 \rightarrow 2\text{AB}$) in the presence of catalyst will be (in kJ mol⁻¹) -

[AIEEE 2007]

- (A) 300 (B) 120 (C) 280 (D) 20

Sol.

Q.19 Consider the reaction, $2\text{A} + \text{B} \rightarrow \text{Products}$. When concentration of B alone was doubled, the half-life of B did not change. When the concentration of A alone was doubled, the rate increased by two times. The unit of rate constant for this reaction is -

[AIEEE 2007]

- (A) L mol⁻¹ s⁻¹ (B) no unit
(C) mol L⁻¹ s⁻¹ (D) s⁻¹

Sol.

Q.20 For a reaction $\frac{1}{2}\text{A} \rightarrow 2\text{B}$, rate of disappearance of 'A' related to the rate of appearance of 'B' by the expression -

[AIEEE 2008]

- (A) $-\frac{d[\text{A}]}{dt} = \frac{1}{4} \frac{d[\text{B}]}{dt}$ (B) $-\frac{d[\text{A}]}{dt} = \frac{d[\text{B}]}{dt}$
(C) $-\frac{d[\text{A}]}{dt} = 4 \frac{d[\text{B}]}{dt}$ (D) $-\frac{d[\text{A}]}{dt} = \frac{1}{2} \frac{d[\text{B}]}{dt}$

Sol.

Q.21 The half life period of a first order chemical reaction is 6.93 minutes. The time required for the completion of 99% of the chemical reaction will be ($\log 2 = 0.301$)

[AIEEE 2009]

- (A) 23.03 minutes (B) 46.06 minutes
(C) 460.6 minutes (D) 230.3 minutes

Sol.

Q.22 The time for half life period of a certain reaction $A \rightarrow \text{products}$ is 1 hour. When the initial concentration of the reactant 'A', is 2.0 mol L^{-1} , how much time does it take for its concentration to come from 0.50 to 0.25 mol L^{-1} if it is a zero order reaction ?

- (A) 4 h (B) 0.5 h (C) 0.25 h (D) 1 h

Sol.

[AIEEE 2010]

Q.23 The rate of a chemical reaction doubles for every 10°C rise of temperature. If the temperature is raised by 50°C , the rate of the reaction increases by about :

[AIEEE 2011]

- (A) 24 times (B) 32 times (C) 64 times (D) 10 times

Sol.

Q.24 For a first order $(A) \rightarrow \text{Products}$, the concentration of A changes from 0.1 M to 0.025 M in 40 minutes. The rate of reaction when the concentration of A is 0.01 M , is :

[AIEEE 2012]

- (A) $3.47 \times 10^{-5} \text{ M/min}$
(B) $1.73 \times 10^{-4} \text{ M/min}$
(C) $1.73 \times 10^{-5} \text{ M/min}$
(D) $3.47 \times 10^{-4} \text{ M/min}$

Sol.

Q.25 The rate of a reaction doubles when its temperature changes from 300 K to 310 K . Activation energy of such a reaction will be:

($R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$ and $\log 2 = 0.301$)

- (A) 58.5 kJ mol^{-1}
(B) 60.5 kJ mol^{-1}
(C) 53.6 kJ mol^{-1}
(D) 48.6 kJ mol^{-1}

[IIT Mains 2013]

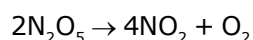
Sol.

LEVEL – II

JEE ADVANCED

OBJECTIVE

2. The rate constant for the reaction



is $3.0 \times 10^{-5} \text{ sec}^{-1}$. If the rate is $2.4 \times 10^{-5} \text{ mol litre}^{-1} \text{ sec}^{-1}$, then the concentration of N_2O_5 (in mol litre^{-1}) is

[JEE SCR 2000]

- (A) 1.4 (B) 1.2 (C) 0.004 (D) 0.8

Sol.

3. If I is the intensity of absorbed light and C is the concentration of AB for the photochemical process

$\text{AB} + h\nu \rightarrow \text{AB}^*$, the rate of formation of AB^* is directly proportional to

[JEE SCR 2001]

- (A) C (B) I
(C) I^2 (D) CI

Sol.

4. Consider the chemical reaction, $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$. The rate of this reaction can be expressed in term of time derivative of concentration of $\text{N}_2(\text{g})$, $\text{H}_2(\text{g})$ or $\text{NH}_3(\text{g})$. Identify the correct relationship amongst the rate expressions.

[JEE SCR 2002]

(A) $\text{Rate} = -\frac{d[\text{N}_2]}{dt} = -\frac{1}{3}\frac{d[\text{H}_2]}{dt} = \frac{1}{2}\frac{d[\text{NH}_3]}{dt}$

(B) $\text{Rate} = -\frac{d[\text{N}_2]}{dt} = -\frac{3d[\text{H}_2]}{dt} = \frac{2d[\text{NH}_3]}{dt}$

(C) $\text{Rate} = \frac{d[\text{N}_2]}{dt} = \frac{1}{3}\frac{d[\text{H}_2]}{dt} = \frac{1}{2}\frac{d[\text{NH}_3]}{dt}$

(D) $\text{Rate} = \frac{d[\text{N}_2]}{dt} = \frac{-d[\text{H}_2]}{dt} = \frac{d[\text{NH}_3]}{dt}$

Sol.

5. In a first order reaction the concentration of reactant decreases from 800 mol/dm^3 to 50 mol/dm^3 in $2 \times 10^4 \text{ sec}$. The rate constant of reaction in sec^{-1} is :

[JEE SCR 2003]

- (A) 2×10^4 (B) 3.45×10^{-5}
(C) 1.3486×10^{-4} (D) 2×10^{-4}

Sol.

6. The reaction, $\text{X} \rightarrow \text{Product}$ follows first order kinetics. In 40 minutes the concentration of X changes from 0.1 M to 0.025 M. Then the rate of reaction when concentration of X is 0.01 M

[JEE SCR 2004]

- (A) $1.73 \times 10^{-4} \text{ M min}^{-1}$ (B) $3.47 \times 10^{-5} \text{ M min}^{-1}$
(C) $3.47 \times 10^{-4} \text{ M min}^{-1}$ (D) $1.73 \times 10^{-5} \text{ M min}^{-1}$

Sol.

7. Which of the following statement is incorrect about order of reaction ? **[JEE 2005]**

- (A) Order of reaction is determined experimentally
(B) It is the sum of power of concentration terms in the rate law expression
(C) It does not necessarily depend on stoichiometric coefficients.
(D) Order of the reaction can not have fractional value.

Sol.

8. Consider a reaction $aG + bH \rightarrow \text{Products}$. When concentration of both the reactants G and H is doubled, the rate increases by eight times. However, when concentration of G is doubled keeping the concentration of H fixed, the rate is doubled. The overall order of the reaction is **[JEE 2006]**

- (A) 0 (B) 1 (C) 2 (D) 3

Sol.

9. Under the same reaction conditions, initial concentration of $1.386 \text{ mol dm}^{-3}$ of a substance becomes half in 40 seconds and 20 seconds through first order and zero order kinetics, respectively. Ratio

$\left(\frac{k_1}{k_0}\right)$ of the rate constants for first order (k_1) and zero order (k_0) of the reactions is **[JEE 2008]**

- (A) $0.5 \text{ mol}^{-1} \text{ dm}^3$ (B) 1.0 mol dm^{-3}
(C) 1.5 mol dm^{-3} (D) $2.0 \text{ mol}^{-1} \text{ dm}^3$

Sol.

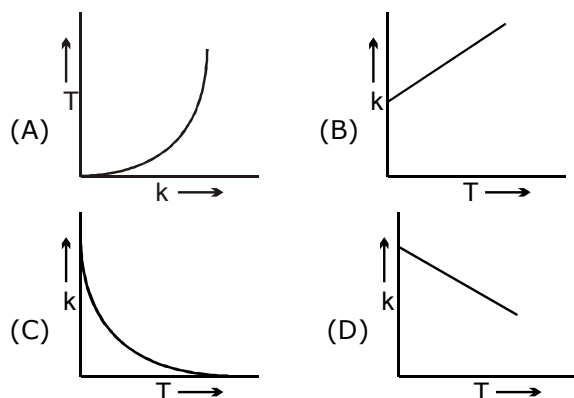
10. For a first order reaction $A \rightarrow P$, the temperature (T) dependent rate constant (k) was found to follow the equation $\log k = - (2000) 1/T + 6.0$. The pre-exponential factor A and the activation energy E_a , respectively, are

- (A) $1.0 \times 10^6 \text{ s}^{-1}$ and 9.2 kJ mol^{-1}
(B) 6.0 s^{-1} and 16.6 kJ mol^{-1}
(C) $1.0 \times 10^6 \text{ s}^{-1}$ and 16.6 kJ mol^{-1}
(D) $1.0 \times 10^6 \text{ s}^{-1}$ and 38.3 kJ mol^{-1}

[JEE 2009]

Sol.

11. Plots showing the variation of the rate constant (k) with temperature (T) are given below. The plot that follows Arrhenius equation is [JEE 2010]



Sol.

12. For the first order reaction [JEE 2011]



- (A) The concentration of the reactant decreases exponentially with time.
- (B) The half-life of the reaction decreases with increasing temperature.
- (C) The half-life of the reaction depends on the initial concentration of the reactant.
- (D) the reaction proceeds to 99.6% completion in eight half-life duration.

Sol.

SUBJECTIVE PROBLEM

14. A hydrogenation reaction is carried out at 500 K. If the same reaction is carried out in the presence of a catalyst at the same rate, the temperature required is 400 K. Calculate the activation energy of the reaction if the catalyst lowers the activation barrier by 20 kJ mol⁻¹. [JEE 2000]

Sol.

15. The rate of first order reaction is 0.04 mole litre⁻¹ s⁻¹ at 10 minutes and 0.03 mol litre⁻¹ s⁻¹ at 20 minutes after initiation. Find the half life of the reaction.

[JEE 2001]

Sol.

16. $2X(g) \rightarrow 3Y(g) + 2Z(g)$

Time (in Min)	0	100	200
Partial pressure of X (in mm of Hg)	800	400	200

Assuming ideal gas condition. Calculate

- (A) Order of reaction
 (B) Rate constant
 (C) Time taken for 75% completion of reaction
 (D) Total pressure when $P_x = 700$ mm. [JEE 2005]

Sol.

17. The concentration of R in the reaction $R \rightarrow P$ was measured as a function of time and the following data is obtained:

[R] (molar)	1.0	0.75	0.40	0.10
t(min.)	0.0	0.05	0.12	0.18

[JEE 2010]

The order of the reaction is

Sol.

18. An organic compound undergoes first-order decomposition. The time taken for its decomposition to $1/8$ and $1/10$ of its initial concentration are $t_{1/8}$ and $t_{1/10}$ respectively.

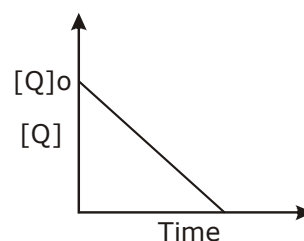
What is the value of $\frac{[t_{1/8}]}{[t_{1/10}]} \times 10$? (take $\log_{10} 2 = 0.3$)

Sol.

[JEE 2012]

19. In the reaction,
 $P + Q \longrightarrow R + S$
 the time taken for 75% reaction of P is twice the time taken for 50% reaction of P. The concentration of Q varies with reaction time as shown in figure. the overall order of the reaction is
 (A) 2 (B) 3 (C) 0 (D) 1

[JEE 2013]



Sol.

Answer-Key

Exercise-I

1. B	2. D	3. B	4. D	5. A	6. B
7. C	8. D	9. B	10. D	11. B	12. C
13. D	14. A	15. B	16. D	17. A	18. A
19. B	20. B	21. B	22. B	23. B	24. C
25. C	26. C	27. C	28. B	29. D	30. D
31. D	32. D	33. A	34. B	35. C	36. D
37. C	38. B	39. A	40. C	41. C	42. C
43. D	44. A	45. B	46. B	47. B	48. C
49. D	50. A				

Exercise-II

1. A	2. A	3. A	4. C	5. C	6. D
7. C	8. C	9. A	10. A,B,D	11. A,B,D	12. A,D
13. C	14. C	15. D	16. A	17. C	18. A
19. B	20. A	21. B			
22. C,D	23. A,B	24. B	4. B,C	25. A,B,C	26. B,C,D
27. A,B,C,D	28. A,B,C	29. B,D	30. A,C	31. B,C	32. A,B,D
33. B,C	34. A,C,D	35. A,B			
36. B	37. A	38. D			
39. C	40. A	41. B	42. C	43. A	44. D
45. A	46. B	47. A	48. D	49. A	
50. A-S, B-QST, C-QRS, D-QS					
51. $A \rightarrow R, B \rightarrow Q, C \rightarrow P, D \rightarrow S$	52. $A \rightarrow S, B \rightarrow R, C \rightarrow P, D \rightarrow Q$				
53. $A \rightarrow P, B \rightarrow Q, S \rightarrow R, T \rightarrow V$					

INTEGER TYPE

54. 2	55. 20	56. 5	57. 10	58. 6	59. 3
60. 3	61. 5	62. 6	63. 2	64. 6	

Exercise-III

1. (a) 0.04 M/sec (b) 0.02
2. (a) 0.019 mol L⁻¹ s⁻¹, (b) 0.037 mol L⁻¹ s⁻¹
3. $2k_1 = k_2 = 4k_3$
4. (i) $\frac{dx}{dt} = k[A][B]^2$, (ii) rate increases by 8 times
5. rate increase by 27 times
6. (i) $r = \frac{1}{4} \frac{d[\text{NO}]}{dt} = 9 \times 10^{-4}$ mol litre⁻¹ sec⁻¹, (ii) 36×10^{-4} mol litre⁻¹ sec⁻¹, (iii) 54×10^{-4} mol litre⁻¹ sec⁻¹
7. (i) 7.2 mol litre⁻¹ min⁻¹, (ii) 7.2 mol litre⁻¹ min⁻¹
8. $\frac{1}{6}$
9. (i) 7.2 M, (ii) 10 M
10. $K = 0.01$ M min⁻¹
11. 0.75 M
12. 6×10^{-9} sec
13. 1.2 hr
14. (i) 36 min, (ii) 108 min.
15. (i) 0.0223 min⁻¹, (ii) 62.17 min
17. 924.362 sec.
18. expiry time = 41 months
19. 3.3×10^{-4} s⁻¹
20. 62.13 min
21. 11.2 %
22. (a) Third order, (b) $r = k[\text{NO}]^2[\text{H}_2]$, (c) 8.85×10^{-3} M sec⁻¹
23. (a) order w.r.t NO = 2 and w.r.t Cl₂ = 1, (b) $r = K[\text{NO}]^2[\text{Cl}_2]$, (c) $K = 8$ L² mol⁻² s⁻¹
(d) rate = 0.256 mole L⁻¹ s⁻¹
24. (i) first order (ii) $k = 1.308 \times 10^{-2}$ min⁻¹ (iii) 73%
25. (i) rate = $[A][B]$; (ii) $k = 4 \times 10^{-2}$ M⁻¹ s⁻¹; (iii) rate = 2.8×10^{-3} M s⁻¹
26. (i) Zero order, (ii) $K = \frac{5\text{Pa}}{\text{s}}$
27. Zero order
28. (a) $n = 1$, (b) $\frac{dx}{dt} = k[\text{CH}_3\text{COCH}_3]$, (c) 8.67×10^{-3} s⁻¹, (d) 1.56×10^{-5} M s⁻¹

29. 166.6 min 30. 5.26%, 4.62×10^5 sec 32. (i) $t = 13.96$ hrs, (ii) 2.2176 litre
33. 54 min 34. 15 min
35. $K = \frac{1}{t} \ln \frac{P_3}{2(P_3 - P_2)}$ 36. $K = \frac{1}{t} \ln \frac{P_3}{(P_3 - P_2)}$ 37. $K = \frac{1}{t} \ln \frac{V_1}{(2V_1 - V_2)}$
38. $K = \frac{1}{t} \ln \frac{4V_3}{5(V_3 - V_2)}$ 39. $K = \frac{1}{t} \ln \frac{r_\infty}{(r_\infty - r_1)}$ 40. $8.12 \times 10^{-6} \text{ Ms}^{-1}$, $0.012 \text{ atm min}^{-1}$
41. (a) 90 mm, (b) 47 mm, (c) 6.49×10^{-2} per minutes, (d) 10.677 min.
42. First order 43. $k_1 = 2.605 \times 10^{-3} \text{ min}^{-1}$
44. (i) $r = K[(\text{CH}_3)_2\text{O}]$, $0.000428 \text{ sec}^{-1}$ 45. First order
46. (a) first order, (b) 13.75 minutes, (c) 0.716
47. 966 min 48. 206.9 min 49. 11.45 days 50. 0.180 atm, 47.69 sec.
51. $\frac{1}{e^{(K_1+K_2)t} - 1}$ 52. $\frac{[C]}{[A]} = \frac{10}{11}(e^{11x} - 1)$ 53. 77.7, 22.3 54. $t = 4$ min
56. 349.1 k 57. $55.33 \text{ kJ mole}^{-1}$ 58. 306 k
59. (a) $2.31 \times 10^{-12} \text{ min}^{-1}$, $6.93 \times 10^{-2} \text{ min}^{-1}$, (b) $43.85 \text{ kJ mole}^{-1}$
60. rate of reaction increases 5.81×10^8 times 61. $10.272 \text{ k cal mol}^{-1}$ 62. 1.585
63. $r = K' [\text{NO}]^2 [\text{Br}_2]$ 64. $r = K [\text{NO}]^2 [\text{H}_2]$, where $K = k_2 \times K_1$
66. (a) $\frac{d(D)}{dt} = \frac{k_1 k_3 (A)(B)}{k_2 + k_3}$; (b) $E_a = E_{a1} + E_{a3} - E_{a2}$, $A = \frac{A_1 A_3}{A_2}$
68. 53.84 69. (a) 6.25 ; (b) 14.3 ; (c) 0% 70. $P_t = 379.55 \text{ mm Hg}$, $t_{7/8} = 399.96 \text{ min}$
71. 0.0207 min^{-1} 72. 15.13 week 73. 0.26 : 1 74. 0.0805

Exercise-IV**Level -1**

1. C 2. D 3. A 4. A 5. D 6. C
7. A 8. A 9. B 10. A 11. D 12. B
13. B 14. A 15. B 16. A 17. C 18. D
19. A 20. A 21. B 22. C 23. B 24. D
25. C

Level -2**OBJECTIVE PROBLEM**

1. 2. D 3. B 4. A 5. C 6. C
7. D 8. D 9. A 10. D 11. A 12. ABD

SUBJECTIVE PROBLEM

13. $3.435 \times 10^{-3} \text{ M/min}$ 14. 100 kJmol^{-1} 15. $t_{1/2} = 24.14 \text{ min}$
16. (B) 1 (B) $6.93 \times 10^{-3} \text{ min}$ (C) 200 min (D) 950 mm 17. 0
18. 0009 19. D

THE KEY**RADIOACTIVITY**

The spontaneous emission of particles, electromagnetic radiation or both by unstable nuclei, is known as radioactivity.

PROPERTIES OF α , β -PARTICLES AND γ -RAYS.

	Properties	Alpha	Beta	Gamma
1	Nature	Fast moving He nuclei	Fast moving electrons	High energy radiations
2	Representation	${}_2\text{He}^4$ or α	${}_{-1}\text{e}^0$ or ${}_{-1}\beta^0$	γ or ${}_0^0\gamma$
3	Charge	2 unit (+ve)	1 unit (-ve)	No charge
4	Velocity	1/10 of light	33% to 90% of light	Same as light waves
5	Relative penetrating power	1 or (0.01 mm of Al foil)	100 or (0.1 cm of Al foil)	10000 or (8 cm lead or 25 cm steel)
6	Travel distance in air	2 – 4 cm	200 – 300 cm	500 m
7	Kinetic energy	high	low	–
8	Effect on ZnS plate	Luminescence	Little effect	–
9	Mass g/particle	6.65×10^{-24}	9.11×10^{-28}	–
10	Relative ionising power	10000	100	1

Nuclear Size

Rutherford's α -scattering experiment revealed. He found that almost all of the mass of an atom (the nuclear mass) is concentrated in a very small volume at its centre, and had high electric charge, which was bound by the short range strong interaction. He curiously found some α -particles bouncing back to the nucleus: it is like 'an artillery shell bouncing off tissue paper'. **$R = r_0 A^{1/3}$, $r_0 = 1.2 \text{ fm}$**

Where A is the atomic mass; experimentally, found to be:

So, for example, for ${}_{238}\text{U}$, $r = 7.4 \text{ fm}$.

Kinetic of nuclear disintegration

►► Radioactive decay is a first order process. Hence $-\frac{dN}{dt} = \lambda N$ or $N = N_0 e^{-\lambda t}$

where N = number of radioactive nuclei at any time t ;

N_0 = number of radioactive nuclei at $t = 0$;

λ = decay constant.

►► **Activity** activity (A) = $-\frac{dN}{dt} = \lambda N$

S.I. units :

Disintegration per second (dps). 1 dps = 1 Bq (Becquerel)

1Ci (Curie) = 3.7×10^{10} dps.

1 Rd (Rutherford) = 10^6 dps

Specific activity = dps / gm

►► **Half life ($t_{1/2}$)** The time taken by half the nuclei (originally present) to decay. $t_{1/2} = 0.693/\lambda$
 Note : After n half-lives have passed, activity is reduced to $\frac{1}{2^n}$ of its initial value.

►► **Average life (t_{av})**

$$T_{avg} = \frac{1}{\lambda} = \frac{t_{1/2}}{0.693} = 1.44 t_{1/2}$$

APPLICATION OF NUCLEAR DISINTEGRATION :

The age of the earth : The age of the earth has been estimated by uranium dating technique. The uranium ore (rock) which is found in nature is associated with non-radioactive lead which is believed to be the end product of radioactive disintegration of uranium. A sample of uranium rock is analysed for ^{238}U and ^{206}Pb contents. From this analysis, let the quantities in mole be

$N = ^{238}\text{U mole}, N_0 = ^{238}\text{U mole} + ^{206}\text{Pb mole}.$

$$\lambda t = 2.303 \log_{10} \frac{N_0}{N} = 2.303 \log_{10} \frac{^{238}\text{U} + ^{206}\text{Pb}}{^{238}\text{U}} = 2.303 \log_{10} \left[1 + \frac{^{206}\text{Pb}}{^{238}\text{U}} \right]$$

The value of 't' can be calculated by putting the value of λ which is equal to $\frac{0.693}{t_{1/2}}$

So,

$$t = \frac{2.303 \times t_{1/2}}{0.693} \log_{10} \left[1 + \frac{^{206}\text{Pb}}{^{238}\text{U}} \right]$$

Here 't' corresponds to the age of earth which has been found to be 4.5 billion years.

Radio carbon dating : By using the half life period of ^{14}C , it is possible to determine the age of various objects. In living material the ratio of ^{14}C to ^{12}C remains relatively constant. When a tissue in an animal or plant dies, ^{14}C decreases because the intake of ^{14}C do not occur. Therefore, in the dead tissue the ratio ^{14}C to ^{12}C would decrease, depending on the age of the tissue.

Thus $\lambda = \frac{2.303}{t} \log_{10} \left(\frac{N_0}{N} \right)$ or $\frac{0.693}{t_{1/2}} = \frac{2.303}{t} \log_{10} \left(\frac{N_0}{N} \right)$

N_0 = Ratio of $\text{C}^{14}/\text{C}^{12}$ in green plant or atmosphere

N = Ratio of $\text{C}^{14}/\text{C}^{12}$ in wood (fossil)

or

N_0 = Activity of green plant per unit mass

N = Activity of wood per unit mass

Although, the method is suitable to a variety of organic materials, accuracy depends on the half life to be used, variations in levels of atmospheric carbon - 14 and contamination.

THEORIES REGARDING NUCLEAR STABILITY

(A) Even odd theory of nuclear stability

The number of stable nuclides is maximum when both p and n are even number, 165 such stable nuclei are known.

p	n	No. of stable nucleus
even	even	165
even	odd	55
odd	even	50
odd	odd	5

(B) Magic numbers and nuclear stability

Nuclei with **2, 8, 20, 28, 50, 82 or 126** protons or neutrons are exceptionally stable and have a larger number of stable isotopes than neighboring nuclei in the periodic table. These numbers are called magic numbers. They are supposed to represent completely filled nuclear shells of energy levels.

e.g. $_{50}^{100}\text{Sn}$ having 10 stable isotopes while $_{51}^{121}\text{Sb}$ has only two stable isotopes.

Nuclei with magic number of protons as well as neutrons have notably high stabilities. [eg.

^4_2He , $^{16}_8\text{O}$, $^{40}_{20}\text{Ca}$ and $^{208}_{82}\text{Pb}$].

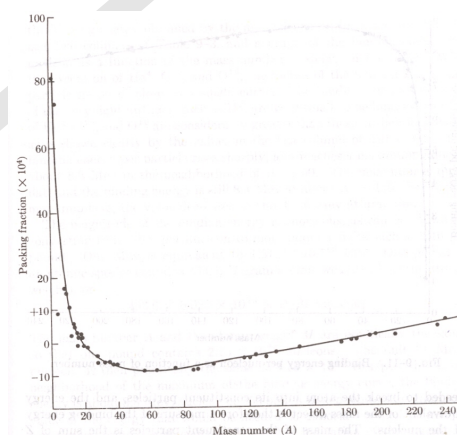
(C) Packing Fraction

'Aston' expressed relation between isotopic mass & mass number in terms of packing fraction.

Packing Fraction

$$= \frac{\text{Atomic mass} - \text{Mass number}}{\text{Mass number}} \times 10^4$$

- * packing fraction of C-12 is exactly zero.
- * packing fraction may be positive or negative
- * negative packing fraction implies that nuclei is stable
- * positive packing fraction implies that nuclei is unstable
- * Some lighter nuclei have positive packing fraction although nucleus is stable
- * Mo, Ru, Rh, Pd have lowest packing fraction



(D) Binding Energy : It is defined energy required to break the nucleus into its component protons & neutrons. Binding energy per nucleon gives a quantitative measure of nuclear stability.

- * Mass defect (Δm) = mass of neutron + mass of proton - mass of nucleus
- Binding energy of nucleus = $\Delta m c^2$

- * The binding energy for a nucleus containing Z protons and N neutrons can be calculated as

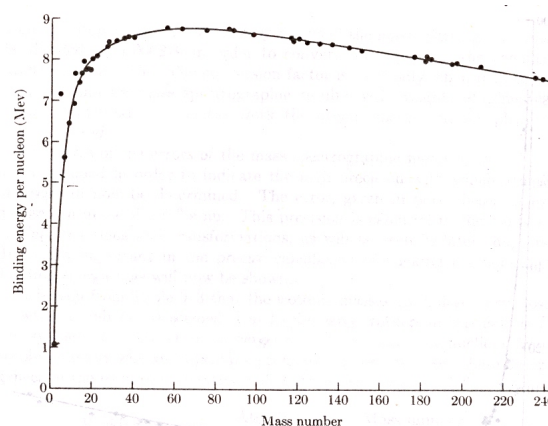
$$\text{Binding energy} = (Zm_H + Nm_n - \frac{A}{Z}M)c^2$$

Note that above equation does not include Zm_p , the mass of Z protons. Rather, it contains ZM_H , the mass of Z protons and Z electrons combined as Z neutral ${}^1_1\text{H}$ atoms, to balance the Z electrons included in ${}_Z^AM$, the mass of the neutral atom.

If $\Delta m = 1 \text{ a.m.u}$ then B.E. = 931.5 MeV

$$\text{B.E. per nucleon} = \frac{\text{B.E.}}{\text{No. of nucleons}}$$

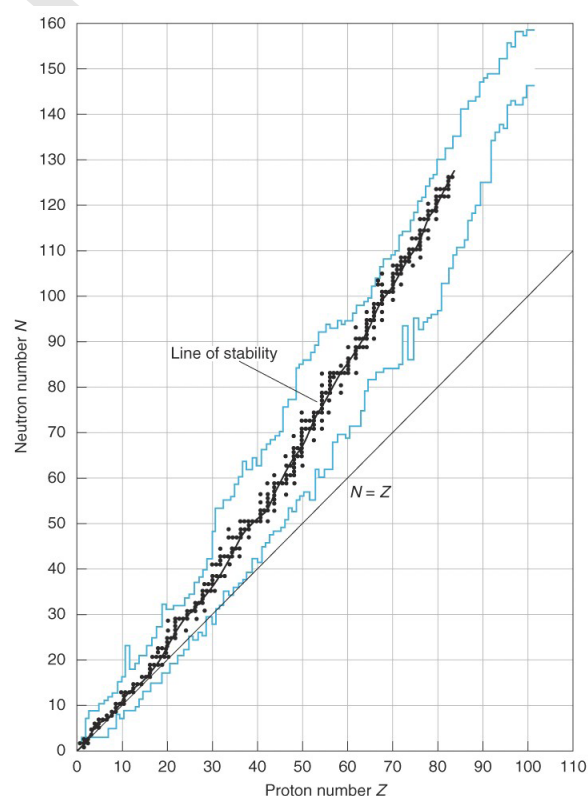
- * A very heavy nucleus, say $A = 240$, has lower binding energy per nucleon compared to that of a nucleus with $A = 120$. Thus if a nucleus $A = 240$ breaks into two $A = 120$ nuclei, energy would be released in the process. This implies nucleons get more tightly bound. It has very important applications for energy production through fission.



- * Consider two very light nuclei ($A \leq 10$) joining to form a heavier nucleus. The binding energy per nucleon of the heavier nuclei is more than the binding energy per nucleon of the lighter nuclei, again energy would be released in such a process of fusion.
- * Nuclear binding energy is maximum for mass number 50 – 60.
- * Fe, Co, Ni very high nuclear binding energy.

(E) Neutron / proton ratio and stability belt

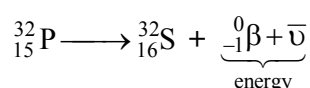
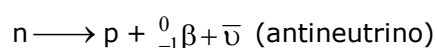
- ▶▶ For atomic number < 20 , most stable nuclei have $n:p$ ratio nearly 1 : 1 (except H & Ar).
- ▶▶ For n/p ratio > 1.52 , nucleus is unstable. Largest stable nucleus is ${}^{209}_{83}\text{Bi}$ for which n/p ratio is 1.52.
- ▶▶ For atomic number > 83 , there are no stable nuclei.



Expected emissions from unstable nucleus:

1. n/p ratio above stability belt :

Those nucleus which have high (lie above the stability belt) undergoes ${}^0_{-1}\beta$ decay.

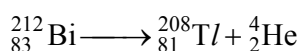


- * Beta decay is possible whenever the mass of the original neutral atom is greater than the final atom.
- * The difference between the rest mass energy of the initial constituents and that of the final products is called the Q-value of the process. Thus, if U_i is the rest mass energy of the initial constituents and U_f is that of the final products,

$$Q = U_i - U_f$$
 Q value is positive i.e. isolated neutron may decay into proton.
- * The energy released is shared by antineutrino and beta particle.
- * The energy of ${}_{-1}^0\beta$ particle can be any thing between zero & Q.
- * Such transformation takes place because of weak forces operating within the nucleus.

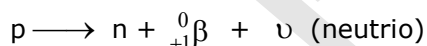
2. n/p ratio below stability belt :

(a) α -decay



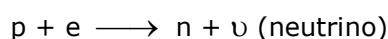
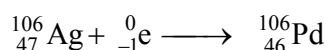
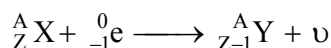
- * Observed in nuclei with $A > 210$
- * Mass number & the atomic number of the daughter nucleus decreases by 4 & 2 respectively compared to parent nucleus.
- * Alpha decay may take place spontaneously or it can be initiated.
- * Alpha decay is possible whenever the mass of the original neutral atom is greater than the sum of the masses of the final neutral atom and the neutral helium-4 atom.
- * All the alpha particles coming from a particular decay reaction have the same kinetic energy.

$({}_{+1}^0\beta)$ Positron decay



- * Those nucleus which have low value of n/p ratio (lie below the stability belt) undergoes ${}_{+1}^0\beta$ decay.
- * Q value is negative i.e. isolated proton will not decay into neutron.
- * Positron decay is possible whenever the mass of the original neutral atom is greater than at least two electron masses larger than the final atom.

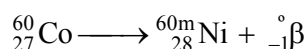
K electron capture

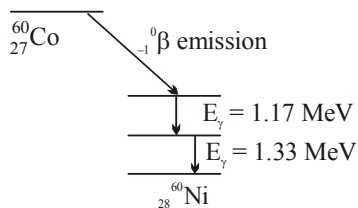
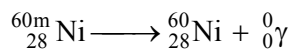


- * Electron capture can occur whenever the mass of original neutral atom is larger than that of final atom.
- * Those nucleus having low n/p ratio can capture K shell electron.
- * X-rays are emitted during the process.

γ -decay

When an α or β decay takes place, the daughter nucleus generally formed is in excited state & comes to ground state by a single or successive transitions by emitting electromagnetic radiations i.e. γ rays.





* Life time of metastable nucleus thus form as life time less than 10^{-9} sec.

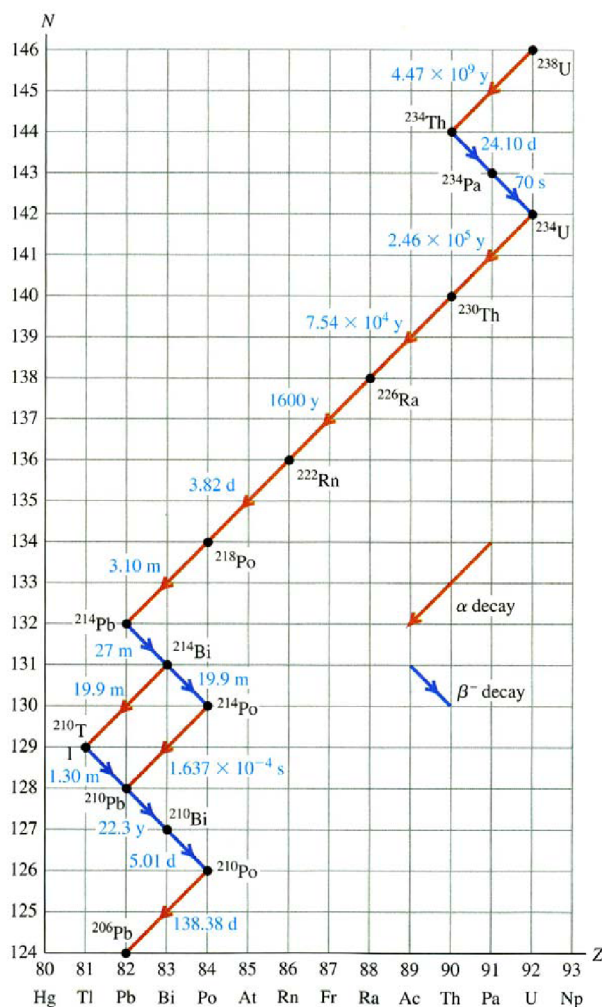
* No. of neutron and proton is unchanged while quantum state of nucleon changes.

RADIOACTIVE DISINTEGRATION SERIES :

Many radioactive nucleus ($Z > 82$) are obtained in nature as a member of natural decay series. The series of nuclear reaction is known as radioactive disintegration series.

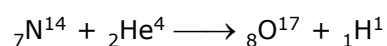
Series	Parent Nucleus	Last Nucleus	No. of α	No. of β
$4n$ or Thorium series	Th^{232}	Pb^{208}	6	4
$(4n+1)$ or Neptunium series	Pu^{241}	Bi^{209}	8	5
$4n+2$ or Uranium series	U^{238}	Pb^{206}	8	6
$4n+3$ or Actinium series	U^{235}	Pb^{207}	7	4

$4n$, $4n + 3$ and $4n + 3$ series are natural while $(4n + 1)$ is artificial.

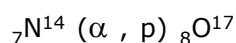


NUCLEAR REACTIONS

The reactions in which nuclei of atoms interact with other nuclei or elementary particles such as α -particle, proton, neutron, deuteron, etc, resulting in the formation of new nuclei with or without liberation of one or more elementary particles, are called nuclear reactions. The particles resulting nuclear reactions are also called projectiles. In all the nuclear reactions, the total number of protons and neutrons are conserved. Nuclear reactions may be expressed as similar as chemical reactions, like

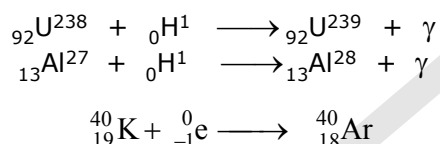
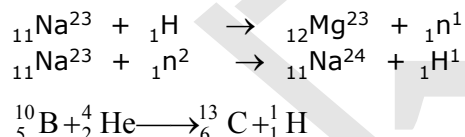
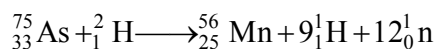
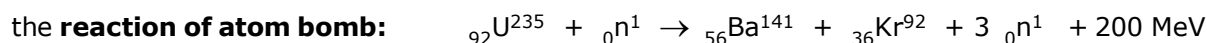


Here, the nucleus of nitrogen atom is converted in to the nucleus of oxygen atom by α -particle and proton is also produced as a by-product. These reactions may be expressed by short hand notation, in which the projectile and the liberating particle are expressed by their symbols, in a small bracket in between the parent and the product nucleus. For example, the above reaction may also be expressed as:

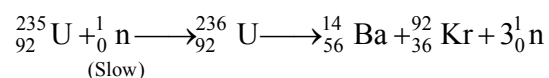


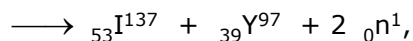
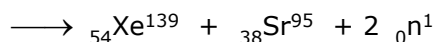
Some differences between nuclear and chemical reactions

No.	Chemical reaction	Nuclear reaction
1.	No new element is formed	New element is formed
2.	Valence electrons of atoms participates	Only the nucleus of atoms participates
3.	Balanced by the conservation of atoms	Balanced by the conservation of nuclear charge and mass number (total number of neutrons and protons)
4.	Mass conservation is obeyed	Disobey mass conservation
5.	May be exothermic or endothermic, liberating or absorbing relatively small amount of energy	May be exothermic or endothermic, liberating or absorbing relatively very high amount of energy
6.	May be reversible	Irreversible
7.	May obey kinetics of any order	Obeys only first order kinetics
8.	Rate depends on external factors like temperature and the catalytic conditions	Rate is independent from any external condition

TYPES OF NUCLEAR REACTIONS:**1. Projectile Capture Reactions:****2. Particle - particle reactions:****3. Spallation reactions:** High speed projectiles with 400Mev bombarded on high nucleus giving smaller nucleus.**4. Fission reactions:** It is the nuclear reaction in which a heavy nucleus is broken down by a slow or thermal neutron (energy about 0.04 eV) into two relatively smaller nuclei with the emission of two or more neutrons and large amount of energy. For example,

It is also found that the products of nuclear fission reactions are not unique. Some more products are formed. The most probable mass numbers of the two nuclides formed are around 95 and 140 and an average of 2.5 neutrons is emitted out per fission.





Fission reactions produce more neutrons than are used to initiate the process. A nuclear fission chain reaction has three general steps:

- (i) Initiation (ii) Propagation (iii) Termination

The destructive action of atom bomb is due to the following reasons:

- (i) As some neutrons are produced in each fission, they may collide efficiently with the other U^{235} nuclei to produce more neutrons and thus the reaction occurs in chain like fashion. It results the emission of a large amount of energy in very small time.
- (ii) Each product of fission is radioactive and hence increases the intensity of radiation in that region, resulting the problems due to radiations.

Chain reaction : –

Whatever are the primary products of fission of uranium, it is certain that neutrons are always set free. If the conditions are so arranged that each of these neutrons can, in turn, bring about the fission, the number of neutrons will increase at a continuously accelerating rate until whole of the material is exhausted. Such type of reaction is called chain reaction. It takes very small time and is uncontrolled. It ends in a terrible explosion due to release of enormous amount of energy. The chain reaction is shown in Fig.

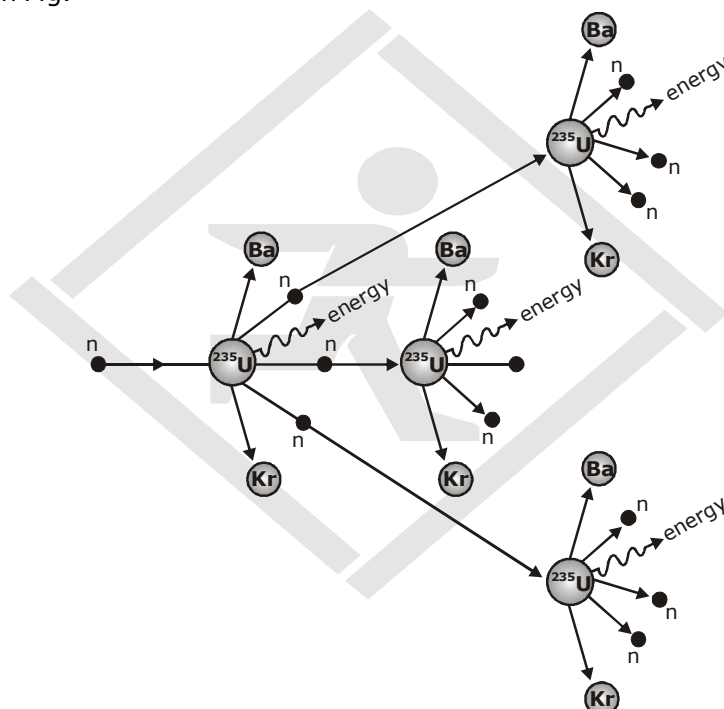
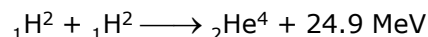


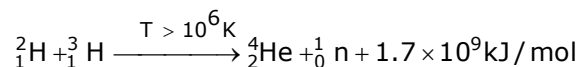
Fig. Chain reaction in Uranium - 235

5. **Fusion reactions:** It is the nuclear reaction in which two or more light nuclei fused together to form heavier nuclei, with the evolution of tremendous amount of energy. In such reactions, relatively more stable nucleus having higher binding energy per nucleon is formed. Such reaction is difficult to occur because when the nuclei of different atoms come closer, they repel each other strongly. This is why, very high temperature of the order 10^6K is needed for the occurrence of such reactions. However, the overall reaction is highly exothermic due to large mass defect. Some examples of nuclear fusion reactions are:

Probable reaction of hydrogen bomb:

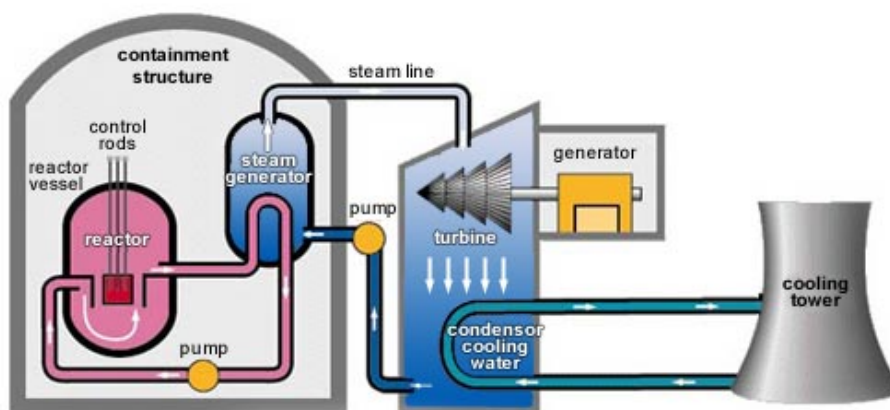


Probable reaction occurring at the surface of sun: $4 {}_1\text{H}^2 \longrightarrow {}_2\text{He}^4 + 2 {}_1\text{e}^0 + 24.7 \text{ MeV}$



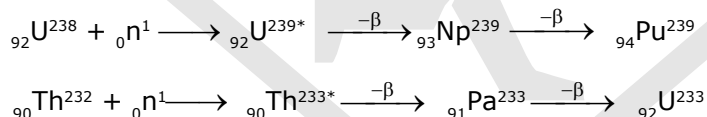
NUCLEAR REACTOR

A nuclear reactor is the furnace, place where nuclear fission reaction is performed to get energy. The essentials of a nuclear reactor are:



1. **Fuel** : Nuclear fuels are of two types:

- (i) **Fissile materials** : These are the nuclides which directly results chain reaction on bombardment with slow neutrons. Such nuclides are U^{235} , Pu^{239} , U^{233} , etc.
- (ii) **Fertile material** : These are the nuclides which are non-fissile, but they may be converted in to a fissile material by the action of neutrons. Such nuclides are U^{238} and Th^{232} .



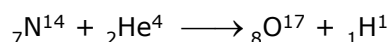
Such conversions are performed in a special type of nuclear reactor called Breeder Reactor.

2. **Moderator**: It is used to slow down the fast neutrons without absorbing them. Example: water, graphite, helium, D_2O etc.
3. **Control rods**: These are the rods of material which can absorb neutrons and hence control the fission reaction. Example: Cadmium, boron, etc.
4. **Coolant**: These are the material which transforms the energy produced in the fission reaction in to heat energy. Example: Liquid alloy of sodium and potassium, heavy water, polyphenyls, etc

ARTIFICIAL TRANSMUTATION

It is the method of conversion of atom of one element in to the atom of other element with the help of some particles like alpha particle, proton, deuteron, neutron, etc (called projectiles). The first such transmutation was performed by Rutherford. When N^{14} atoms were bombarded by very fast moving

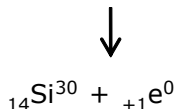
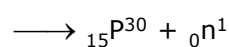
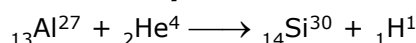
α -particles, the nitrogen atom has changed into oxygen atom and proton is produced simultaneously



Later on, Rutherford and Chadwick shown that most of the nuclei may be transmuted by the suitable projectile. After the discovery of cyclotron, a particle accelerating machine, such transmutations become more easier.

ARTIFICIAL RADIOACTIVITY

When Irene Curie and F. Joliot bombarded the atoms of Al^{27} , B^{10} or Mg^{24} by fast moving α -particles, protons, neutrons and positrons were produced. They observed that the emission of protons and neutrons stop on stopping the bombardment but the emission of positron continues. They also observed that the rate of emission of positron decreases exponentially in the manner similar to natural radioactivity. They named the isotope emitting positron as **artificial radioisotope** and the phenomenon as **artificial radioactivity**.



NUCLEAR TRANSMUTATION

An experiment performed by Rutherford in 1919, however, suggested the possibility of producing radioactivity artificially. When he bombarded a sample of nitrogen with α particles, the following reaction took place:



An oxygen-17 isotope was produced with the emission of a proton. This reaction demonstrated for the first time the feasibility of converting one element into another, by the process of nuclear transmutation. Nuclear transmutation differs from radioactive decay in that the former is brought about by the collision of two particles.

TRANSURANIUM ELEMENTS

Particle accelerators made it possible to synthesize the so-called transuranium elements, elements with atomic numbers greater than 92. Neptunium ($Z = 93$) was first prepared. Since then, many other transuranium elements have been synthesized. All isotopes of these elements are radioactive.

NEUTRON ACTIVATION ANALYSIS

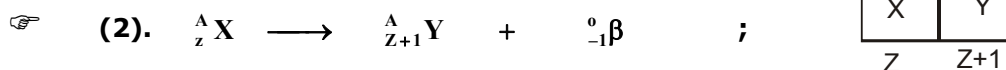
Quantities of elements that are too small for chemical analysis can be detected by this method. When bombarded with neutrons, many stable nuclides absorb a neutron to become unstable & then undergo ${}^0_{-1}\beta$ decay. The energies of ${}^0_{-1}\beta$ & ${}^0_0\gamma$ depend on the unstable nuclide & provide a means of identifying its original stable nuclide.

Soddy Fajjan Rule or Group Displacement Law



Parent Nucleus Daughter Nucleus α - particle

☞ When an α - particle is emitted, the daughter nuclei formed is shifted two positions left in the periodic table with respect to the parent nuclei.



Parent Nucleus Daughter Nucleus β - particle

☞ After emission of β - particle daughter nucleus shifts one position right in the periodic table.

Level

n=1

n=2

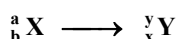
n=3

etc.

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Calculation of α and β Particles

⇒ **GENERAL CASE**



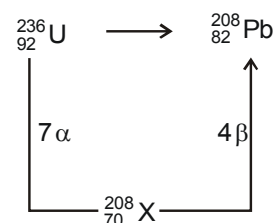
⇒ **No. of α -particles = $\frac{a-y}{4}$**

⇒ **No. of β - particles = $(x - b) + \frac{(a - y)}{2}$ or**

⇒ **No. of β - particles = $\frac{1}{2}$ No. of α particles
- (b-x)**

⇒ **SPECIAL CASE**

⇒ **Example :**



TYPES OF NUCLEI

(1) Isotopes species : Same atomic number but different mass number

Example :

(i) ${}^1_1\text{H}$ (Protium), ${}^2_1\text{H}$ (Deuterium) and ${}^3_1\text{H}$ (tritium)

(ii) ${}^{14}_6\text{C}$ and ${}^{12}_6\text{C}$

(iii) ${}^{10}_5\text{B}$ and ${}^{11}_5\text{B}$

(iv) ${}^{35}_{17}\text{Cl}$ and ${}^{37}_{17}\text{Cl}$

(v) ${}^{28}_{14}\text{Si}$ and ${}^{29}_{14}\text{Si}$ and ${}^{30}_{14}\text{Si}$

(2) Isoelectronic species :

Same valence electron & same number of atoms

Example : (i) $\text{Ne} = 1s^2 2s^2 2p^6 = 10 e^-$

$\text{O}^{2-} = 1s^2 2s^2 2p^6 = 10 e^-$

Ne and O^{2-} are isoelectronic, CO & N_2 are isoelectronic

(3) Isobar species : Same atomic mass but different atomic number

Example : ${}^{41}_{19}\text{K}$ and ${}^{41}_{20}\text{Ca}$ and ${}^{41}_{21}\text{Sc}$

(4) Isotone : Same number of neutrons

Example ; ${}^{14}_6\text{C}$ and ${}^{16}_8\text{O}$

$n_n = 14 - 6 = 8$, $n_n = 16 - 8 = 8$

(5) Isosters species : Same number of atoms and same number of electrons

Example :	Isosters	No. of atom	No. of electrons
	CO_2	3	22
	N_2O	3	22

(6) Isodiaphers species : Difference of neutron and proton is same.

Example : (i) ${}^{208}_{82}\text{Pb} \longrightarrow n = 208 - 82 = 126$, $p = 82 \Rightarrow n - p = 126 - 82 = 44$

${}^{210}_{83}\text{Bi} \longrightarrow n = 210 - 83 = 127$, $p = 83 \Rightarrow n - p = 127 - 83 = 44$

(7) Nuclear isomers :

Nucleus with Same atomic mass, same atomic number and different radioactive properties are called Nuclear isomers.

SOLVED SUBJECTIVE

Problem : 1

In an ore containing Uranium, the ratio of U^{238} to Pb^{206} nuclei is 3. Calculate the age of the ore, assuming that all the lead present in the ore is the final stable product of U^{238} . The half life of U^{238} is 4.5×10^9 years.

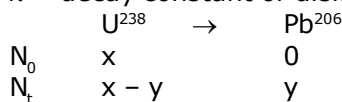
Sol. Note : The radio active decay follows first order kinetics. Here we take $N_0 = C_0$ and $N_t = C_t$ and $\lambda = k$
The first order rate equation for radioactive decay is :

$$\lambda t = 2.303 \log \frac{N_0}{N_t} \quad \text{where } \lambda = \frac{0.693}{t_{1/2}}$$

N_0 = initial nuclei (at $t = 0$)

N_t = final nuclei (at t)

λ = decay constant or disintegration constant



$$\Rightarrow \frac{N_0}{N_t} = \frac{x}{x-y}$$

Using $\lambda t = 2.303 \log \frac{N_0}{N_t}$

Given : $\frac{x-y}{y} = 3 \Rightarrow \frac{x}{x-y} = \frac{4}{3}$

$$\Rightarrow t = \frac{2.303}{0.693} \times 4.5 \times 10^9 \log \frac{4}{3} \Rightarrow t = 1.85 \times 10^9 \text{ years.}$$

Problem : 2

The nucleidic ratio of ${}_1H^3$ to ${}_1H^1$ in a sample of water is 8.0×10^{-18} : 1. Tritium undergoes decay with a half life period of 12.3 years. How many tritium atoms would a 10.0 gm of such sample contain 40 years after the original sample is collected ? [IIT-1992]

Sol. The ratio of tritium atom to that of H-atom will be same as the ratio of moles of T-atoms to that of H-atoms, since 1 mole of $T_2O \equiv 2$ mole of T atoms and 1 mole of $H_2O \equiv 2$ mole of H atoms
Calculate the mass ratio

$$\frac{\text{mass of } T_2O}{\text{mass of } H_2O} = \left(\frac{8 \times 10^{-18} \times 22}{1 \times 18} \right)$$

$$\Rightarrow \text{mass of } T_2O \text{ atoms in 10 gm sample} = \left(\frac{8 \times 10^{-18} \times 22}{22 \times 8 \times 10^{-18} + 1 \times 18} \right) \times 10 = 9.78 \times 10^{-17} \text{ gm}$$

$$\Rightarrow \text{no. of } T_2O \text{ atoms} = \frac{9.78 \times 10^{-17}}{22} \times 6 \times 10^{23} = 2.67 \times 10^6 \text{ atoms}$$

Now using 1st order kinetics rate expression

$$\lambda t = 2.303 \log_{10} \frac{N_0}{N_t} \quad \text{or} \quad \frac{0.693}{12.3} \times 40 = 2.303 \log_{10} \frac{2.67 \times 10^6}{N_t} \quad \text{or} \quad N_t = 2.81 \times 10^5$$

$$\Rightarrow \text{number of } T_2O \text{ atoms after 40 years} = 2.81 \times 10^5$$

1 mole $T_2O \equiv 2$ moles of T-atoms

$$\Rightarrow \text{number of tritium atom after 40 years} = 2 \times 2.81 \times 10^5 = 5.62 \times 10^5$$

Problem : 3

${}^{227}Ac$ has a half-life of 22.0 years with respect to radioactive decay. The decay follows two parallel paths, one leading to ${}^{222}Th$ and the other to ${}^{223}Fr$. The percentage yields to these two daughter nuclides are 2.0 and 98.0 respectively. What are the decay constants (λ) for each of the separate paths?

Sol. The rate constant of the decay is

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{22}$$

If k_1 and k_2 are the rate constant of the reactions leading to ^{222}Th and ^{223}Fr , respectively we have

$$k_1 + k_2 = \frac{0.693}{22}, \quad \frac{k_1}{k_2} = \frac{2}{98}$$

On solving for k_1 and k_2 , we get

$$k_2 = 0.03087 \text{ y}^{-1}, \quad k_1 = 0.00063 \text{ y}^{-1}$$

Problem : 4

On analysis a sample of Uranium was found to contain 0.277 g of $_{82}\text{Pb}^{206}$ and 1.667 g of $_{92}\text{U}^{238}$. The half life period of $_{92}\text{U}^{238}$ is 4.51×10^9 years. If all the lead were assumed to have come from decay of $_{92}\text{U}^{238}$, what is the age of the earth?

Sol. $_{92}\text{U}^{238} = 1.667 \text{ g} = \frac{1.667}{238} \text{ mole}$

$$_{82}\text{Pb}^{206} = 0.227 \text{ g} = \frac{0.227}{206} \text{ mole}$$

\therefore All the lead have come from decay of U.

$$\therefore \text{Moles of Pb formed} = \frac{0.227}{206}$$

$$\therefore \text{moles of U decayed} = \frac{0.227}{206}$$

$$\therefore \text{Total moles of Uranium present initially} = \frac{1.667}{238} + \frac{0.227}{206}, \text{ i.e., } N_0$$

$$\text{Also } N \text{ for } \text{U}^{238} = \frac{1.667}{238}$$

$$\therefore \text{ for } \text{U}^{238}, t = \frac{2.303}{K} \log \frac{N_0}{N} = \frac{2.303 \times 4.51 \times 10^9}{0.693} \log \frac{\frac{1.667}{238} + \frac{0.227}{206}}{\frac{1.667}{238}}, \quad t = 1.143 \times 10^9 \text{ yrs.}$$

Problem : 5

A mixture of ^{239}Pu and ^{240}Pu has a activity of $6.0 \times 10^9 \text{ dis/s}$. The half lives of isotopes are 2.44×10^4 and 6.58×10^3 years, respectively. Calculate the isotopic composition of this sample.

Sol. Total activity of a sample is the sum of the individual activities of all its components.

Let the total mass of the sample be 1 gm and the mass of ^{239}Pu be x gm

$$\therefore \frac{x}{239} \times 6.023 \times 10^{23} \times \frac{0.693}{2.44 \times 10^4} + \frac{(1-x)}{240} \times 6.023 \times 10^{23} \times \frac{0.693}{6.58 \times 10^3}$$

$$= 6 \times 10^9 \times 365 \times 24 \times 60 \times 60$$

On calculating, $x = 0.3896$

$$\therefore ^{239}\text{Pu} = 38.96\% \text{ and } ^{240}\text{Pu} = 61.04\%$$

Problem : 6

A radioactive element A says to B " I am half of what you were when you are one fourth of what I was. Moreover I was 1.414 time than what you were. "If the half life of A is 8 days, what is the half life of B?

Sol. Let the initial number of nuclide of X be x_0
 Let the initial number of nuclide of Y be y_0
 Let the number of nuclide of X after time t be x_t
 Let the number of nuclide of Y after time t be y_t
 $\therefore x_t = \frac{1}{2}y_0$; $y_t = \frac{1}{4}x_0$
 $x_0 = 1.414 y_0$

$$\text{Now, } x_t = x_0 e^{-\lambda_1 t} = \frac{1}{2} y_0 \quad \dots\dots\dots (1)$$

$$y_t = y_0 e^{-\lambda_2 t} = \frac{1}{4} x_0 \quad \dots\dots\dots (2)$$

Dividing equation. (1) by (2)

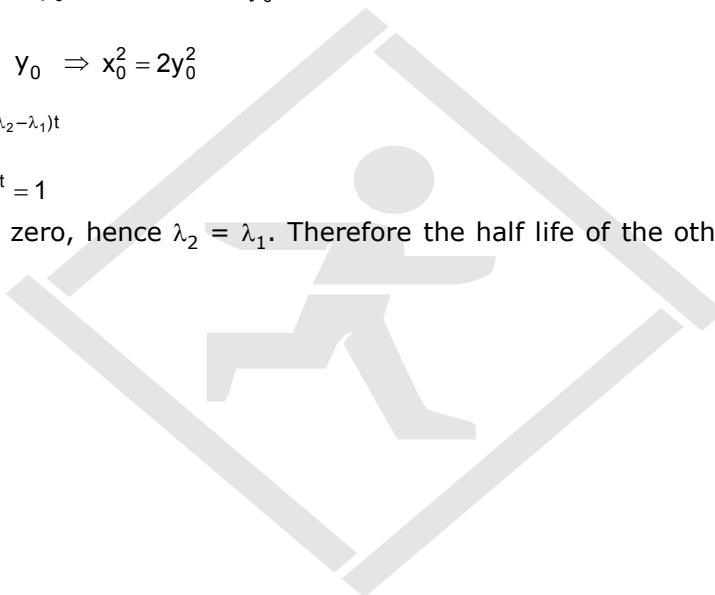
$$\frac{2y_0}{x_0} = \frac{x_0 e^{(\lambda_2 - \lambda_1)t}}{y_0} \Rightarrow 2 = \frac{x_0^2}{y_0^2} e^{(\lambda_2 - \lambda_1)t}$$

$$\text{since } x_0 = \sqrt{2} y_0 \Rightarrow x_0^2 = 2y_0^2$$

$$\therefore 2 = 2e^{(\lambda_2 - \lambda_1)t}$$

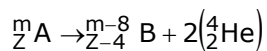
$$\therefore e^{(\lambda_2 - \lambda_1)t} = 1$$

Since t is not zero, hence $\lambda_2 = \lambda_1$. Therefore the half life of the other radioactive element is also **8 days.**



Class Room Problems

Problems : 1 One mole of A present in a closed vessel undergoes decay as:



What will be the volume of helium gas collected at STP after 20 days ($t_{1/2}$ of A = 10 days)?

Sol.

Problems : 2 ${}^{131}\text{I}$ has half life Period 13.3 hour. After 79.8 hour, what fraction of ${}^{131}\text{I}$ will remain?

Sol.

Problems : 3 What mass of ${}^{226}\text{Ra}$, whose $t_{1/2} = 1620$ yrs will give the activity of 1 millicurie?

Sol.

Problems : 4 A radioactive nuclide is produced at a constant rate of ' α ' per second. Its decay constant λ . If N_0 be the number of nuclei at time $t = 0$, then what will be the maximum number of possible nuclei?

Sol.

Problems : 5 The half life of ${}^{212}\text{Pb}$ is 10.6 hour. It undergoes decay to its daughter (unstable) element ${}^{212}\text{Bi}$ of half life 60.5 minute. Calculate the time at which the daughter element will have maximum activity.

Sol.

Problems : 6 A radioactive isotope is being produced at a constant rate x . Half life of the radioactive substance is 'y'. After sometime, the number of radioactive nuclei becomes constant, the value of this constant is

Sol.

Sol.

Problems : 7 ${}_{92}^{238}\text{U}$ by successive radioactive decay changes to ${}_{82}^{206}\text{Pb}$. A sample of uranium ore was analysed and found to contain 1.0 g of ${}_{92}^{238}\text{U}$ and 0.1 g of ${}_{82}^{206}\text{Pb}$. Assuming that all ${}_{82}^{206}\text{Pb}$ has accumulated due to decay of ${}_{92}^{238}\text{U}$, find the age of the ore (half life of ${}_{92}^{238}\text{U} = 4.5 \times 10^9$ yrs).

Sol.

Problems : 9 Prove that time required for 99.9% decay of a radioactive species is almost ten times its half life period.

Sol.

Problems : 8 Calculate the mass of C^{14} (half life = 5720 years) atoms which give 3.7×10^7 disintegrations per second.

Problems : 10 Half life of a radioactive substance A is two times the half life of another radioactive substance B. Initially the number of nuclei of A and B are N_A and N_B respectively. After three half lives of 'A', number of nuclei of both become equal. The ratio of

$\frac{N_A}{N_B}$ will be:

Sol.

Sol.

Problems : 11 1.0 g of $^{198}_{79}\text{Au}$ ($t_{1/2} = 65$ hours) decays by β -emission to produce mercury.

(a) Write the nuclear reaction for process.

(b) How much mercury will be present after 260 hour

Sol.

Problems : 13 1 milligram radium has 2.68×10^{18} atoms. Its half life period is 1620 years. How many radium atoms will disintegrate from 1 milligram of pure radium in 3240 years?

Sol.

Problems : 14 A certain radioisotope ^A_ZX (Half life = 10 days) decays to $^{A-4}_{Z-2}\text{Y}$. If 1 g atom of ^A_ZX is kept in sealed vessel, how much helium will accumulate in 20 days?

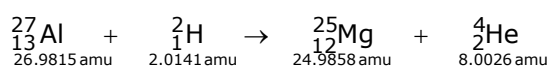
Sol.

Problems : 12 Calculate the probability (P) of survival of a radioactive nucleus for one mean life.

Problems : 15 Binding energy per nucleon of ${}^2_1\text{H}$ and ${}^4_2\text{He}$ are 1.1 MeV and 7 MeV respectively. Calculate the amount of energy released in the following process: ${}^2_1\text{H} + {}^2_1\text{H} \rightarrow {}^4_2\text{He}$

Sol.

Problems : 16 Calculate the energy associated with the following nuclear reaction :



Sol.

Problems : 17 A radioactive isotope ${}_Z\text{A}^m$ ($t_{1/2} = 10$ days) decays to give ${}_{Z-6}\text{B}^{m-12}$ stable atom along with α -particles. If m gm of 'A' are taken and kept in a sealed tube, how much 'He' will accumulate in 20 days at STP?

Sol.

Problems : 18 A sample of pitchblende is found to contain 50% uranium and 2.425% of lead. Of this lead only 93% was Pb^{206} isotope. If the disintegration constant is $1.52 \times 10^{-10} \text{ yr}^{-1}$, how old could be the pitchblende deposits?

Sol.

Problems : 19 On analysis, a sample of uranium ore was found to contain 0.277 g of ${}_{82}\text{Pb}^{206}$ and 1.667 g of ${}_{92}\text{U}^{238}$. The half life period of U^{238} is 4.51×10^9 yrs. If all the lead were assumed to have come from decay of ${}_{92}\text{U}^{238}$, what is the age of the earth ?

Sol.

Problems : 20 ${}_{19}\text{K}^{40}$ consists of 0.012% potassium in nature. The human body contains 0.35% potassium by weight. Calculate the total radioactivity resulting from ${}_{19}\text{K}^{40}$ decay in a 75 kg human body. Half life of ${}_{19}\text{K}^{40}$ is 1.3×10^9 years.

Sol.

Problems : 21 The sun radiates energy at the rate of $4 \times 10^{26} \text{ J sec}^{-1}$. If the energy of fusion process is 27 MeV, Calculate the amount of hydrogen that would be consumed per day for the given process.

Sol.

Problems : 22 A radioactive isotope X with half life of 1.37×10^9 years decays to Y, which is stable. A sample of rock from moon was found to contain both the elements X and Y in the ratio 1 : 7. What is the age of the rock?

Sol.

Problems : 23 A sample of radioactive substance shows an intensity of 2.3 millicurie at a time 't' and an intensity of 1.62 millicurie, 600 seconds later. What is the half life period of the radioactive material?

Sol.

EXERCISE – I**OBJECTIVE PROBLEMS (JEE MAIN)**

1. ${}_{13}^{27}\text{Al}$ is a stable isotope. ${}_{13}^{29}\text{Al}$ is expected to disintegrated by

- (A) α emission (B) ${}_{-1}^0\beta$ emission
(C) Positron emission (D) Proton emission

Sol.

2. Loss of a β -Particle is equivalent to

- (A) Increase of one proton
(B) Decrease of one neutron
(C) Both (A) and (B)
(D) None of these .

Sol.

3. Two radioactive material A_1 and A_2 have decay constants of $10\lambda_0$ and λ_0 . If initially they have same

number of number of nuclei, then after time $\frac{1}{9\lambda_0}$ the ratio of number of their undecayed nuclei will be

- (A) $\frac{1}{e}$ (B) $\frac{1}{e^2}$ (C) $\frac{1}{e^3}$ (D) $\frac{\sqrt{e}}{1}$

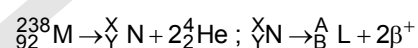
Sol.

4. The half - life of a radioactive isotope is three hours. If the initial mass of isotope were 256 g , the mass of it remaining undecayed after 18 hours would be :

- (A) 16.0 g (B) 4.0 g (C) 8.0 g (D) 12.0 g

Sol.

5. Consider the following nuclear reactions.



The number of neutrons in the element L is

- (A) 142 (B) 144 (C) 140 (D) 146

Sol.

6. The half-life of a radioisotope is four hours. If the initial mass of the isotope was 200 g, the mass remaining after 24 hours undecayed is

- (A) 1.042 g (B) 2.084 g
(C) 3.125 g (D) 4.167 g

Sol.

7. Helium nuclei combine to form an oxygen nucleus. The energy released per nucleon of oxygen nucleus is if $m_O = 15.834$ amu and $m_{He} = 4.0026$ amu

- (A) 10.24 MeV (B) 0 MeV
(C) 5.24 MeV (D) 4 MeV

Sol.

8. A radioactive element gets spilled over the floor of a room. Its half-life period is 30 days. If the initial activity is ten times the permissible value, after how many days will it be safe to enter the room?

- (A) 1000 days (B) 300 days
(C) 10 days (D) 100 days

Sol.

9. Which of the following nuclear reactions will generate an isotope?

- (A) neutron particle emission
(B) positron emission
(C) α -particle emission
(D) β -particle emission

Sol.

10. Read the following :

- (i) The half-life period of a radioactive element X is same as the mean-life time of another radioactive element Y. Initially both of them have the same number of atoms. Then Y will decay at a faster rate than X.
(ii) The electron emitted in beta radiation originates from decays of a neutron in a nucleus
(iii) The half-life of ^{215}At is 100 ms. The time taken for the radioactivity of a sample of ^{215}At to decay to $1/16^{\text{th}}$ of its initial value is 400 ms.
(iv) The volume (V) and mass (m) of a nucleus are related as $V \propto m$.
(v) Given a sample of Radium - 226 having half-life of 4 days. Find the probability, a nucleus disintegrates within 2 half-lives is $3/4$.

Select the correct code for above.

- (A) TTTT (B) TFTF (C) FTFT (D) FTTT

Sol.

11. The radioactive sources A and B of half lives of t hr and $2t$ hr respectively, initially contain the same number of radioactive atoms. At the end of t hours, their rates of disintegration are in the ratio:

- (A) $2\sqrt{2} : 1$ (B) $1 : 8$ (C) $\sqrt{2} : 1$ (D) $\ln 2 : 1$

Sol.

12. The ratio of C^{14} in a living matter is measured to be $\frac{C^{14}}{C^{12}} = 1.3 \times 10^{-12}$ at the present time. Activity of 12.0 gm carbon sample is 180 dmp. The half life of C^{14} is nearly $\times 10^{12}$ sec. **Given: $N_A = 6 \times 10^{23}$**

- (A) 0.18 (B) 1.8 (C) 0.384 (D) 648

Sol.

13. The analysis of a mineral of uranium reveals that ratio of mole of ^{206}Pb and ^{238}U in sample is 0.2. If effective decay constant of process $^{238}\text{U} \rightarrow ^{206}\text{Pb}$ is λ then age of rock is

(A) $\frac{1}{\lambda} \ln \frac{5}{4}$ (B) $\frac{1}{\lambda} \ln \left(\frac{5}{1} \right)$

(C) $\frac{1}{\lambda} \ln \frac{4}{1}$ (D) $\frac{1}{\lambda} \ln \left(\frac{6}{5} \right)$

Sol.

14. Which of the following processes represents a gamma -decay?

- (A) $^AX_Z + \gamma \rightarrow ^AX_{Z-1} + a + b$ (B) $^AX_Z + {}^1_0n_0 \rightarrow ^{A-3}X_{Z-2} + c$
(C) $^AX_Z \rightarrow ^AX_Z + f$ (D) $^AX_Z + e_{-1} \rightarrow ^AX_{Z-1} + g$

Sol.

15. Select correct statment(s):

- (A) The emission of gamma radiation involves transition between energy levels within the nucleus.
(B) ${}^4_2\text{He}$ is formed due to emission of beta particle from tritium ${}^3_1\text{H}$.
(C) When positron (${}^0_{+1}\text{e}$) is emitted, $\frac{n}{p}$ ratio increases.
(D) In general, adsorption is exothermic process.

Sol.

16. Let F_{pp} , F_{pn} and F_{nn} denote the magnitudes of net force by a proton on a proton, by a proton on a neutron and by a neutron on a neutron respectively. Neglect gravitational force. When the separation is 1 fm,

- (A) $F_{pp} > F_{pn} = F_{nn}$ (B) $F_{pp} = F_{pn} = F_{nn}$
 (C) $F_{pp} > F_{pn} > F_{nn}$ (D) $F_{pp} < F_{pn} = F_{nn}$

Sol.

17. The half life of Tc^{99} is 6.0 hr. The delivery of a sample of Tc^{99} from the reactor to the nuclear macular medicine lab of a certain hospital takes 3.0 hr. What is the minimum amount of Tc^{99} that must be shipped in order for the lab to receive 10.0 mg?

- (A) 20.0 mg (B) 15.0 mg (C) 14.1 mg (D) 12.5 mg

Sol.

18. A sample contains 0.1 gram-atom of radioactive isotope A_ZX ($t_{1/2} = 5$ days.) How many number of atoms will decay during eleventh day? [N_A = Avogadro's number]

- (A) $0.1 \left(-e^{-\frac{0.693 \times 11}{5}} + e^{-\frac{0.693 \times 10}{5}} \right)$
 (B) $0.1 \left(-e^{-\frac{0.693 \times 11}{5}} + e^{-\frac{0.693 \times 10}{5}} \right)$
 (C) $0.1 \left(-e^{-\frac{0.693 \times 11}{5}} + e^{-\frac{0.693 \times 10}{5}} \right) N_A$
 (D) $0.1 \left(-e^{-\frac{0.693 \times 11}{5}} + e^{-\frac{0.693 \times 10}{5}} \right) N_A$

Sol.

19. The average (mean) life at a radio nuclide which by parallel path is

$$A \xrightarrow{\lambda_1} B ; \lambda_1 = 1.8 \times 10^{-2} \text{ sec}^{-1}$$

$$2A \xrightarrow{\lambda_2} C ; \lambda_2 = 10^{-3} \text{ sec}^{-1}$$

- (A) 52.63 sec (B) 500 sec (C) 50 sec (D) None

Sol.

20. Two radioactive nuclides A and B have half lives of 50 min and 10 min respectively. A fresh sample contains the nuclides of B to be eight time that of A. How much time should elapse so that the number of nuclides of A becomes double of B

- (A) 30 (B) 40 (C) 50 (D) None

Sol.

21. A sample of $^{14}\text{CO}_2$ was to be mixed with ordinary CO_2 for a biological tracer experiment. In order that 10 cm^3 of diluted gas should have 10^4 dis/min, what activity (in μCi) of radioactive carbon is needed to prepare 60 L of diluted gas at STP.

[$1\text{ Ci} = 3.7 \times 10^{10}\text{ dps}$]

- (A) 270 μCi (B) 27 μCi (C) 2.7 μCi (D) 2700 μCi

Sol.

22. Wooden article and freshly cut tree show activity of 7.6 and $15.2\text{ min}^{-1}\text{ gm}^{-1}$ of carbon ($t_{1/2} = 5760$ years) respectively. The age of article in years, is

- (A) 5760 (B) $5760 \times \left(\frac{15.2}{7.6}\right)$
(C) $5760 \times \left(\frac{7.6}{15.2}\right)$ (D) $5760 \times (15.2 - 7.6)$

Sol.

23. A radioactive sample has an initial activity of 56 dpm (disintegration per min). After 69.3 min it was found to have an activity of 28 dpm. Find the number of atoms in a sample having an activity of 10 dpm.

- (A) 693 (B) 1000 (C) 100 (D) 10,000

Sol.

24. The radioactivity of a sample is R_1 at a time T_1 and R_2 at a time T_2 . If the half life of the specimen is T , the number of atoms that have disintegrated in the time $(T_2 - T_1)$ is equal to

- (A) $(R_1 T_1 - R_2 T_2)$ (B) $(R_1 - R_2)$
 (C) $(R_1 - R_2)/T$ (D) $(R_1 - R_2)T/0.693$

Sol.

25. C^{14} is a beta active nucleus. A sample of $C^{14} H_4$ gas kept in a closed vessel shows increase in pressure with time. This is due to

- (A) The formation of $N^{14} H_3$ and H_2
 (B) The formation of $B^{11} H_3$ and H_2
 (C) The formation of $C^{14}_2 H_4$ and H_2
 (D) The formation of $C^{12} H_3$, $N^{14} H_2$ and H_2

Sol.**Comprehension**

Nuclei of a radioactive element 'A' are being produced at a constant rate, α . The element has a decay constant, λ . At time, $t = 0$, there are N_0 nuclei of the element.

26. The number of nuclei of A at time 't' is

- (A) $\frac{\alpha}{\lambda}(1 - e^{-\lambda t})$ (B) $N_0 \cdot e^{-\lambda t}$
 (C) $\frac{1}{\lambda}[\alpha - (\alpha - \lambda N_0)e^{-\lambda t}]$ (D) $\frac{N_0 \cdot \alpha}{\lambda} \left[1 - \left(1 - \frac{\lambda}{\alpha} \right) e^{-\lambda t} \right]$

Sol.

27. If $\alpha = 2N_0\lambda$, the number of nuclei of A after one half life of A becomes

- (A) zero (B) $2N_0$ (C) $1.5 N_0$ (D) $0.5 N_0$

Sol.

28. If $\alpha = 4N_0\lambda$, the number of nuclei of A when A has reached steady state:

- (A) Zero (B) $4N_0$ (C) $1.5 N_0$ (D) N_0

Sol.

Sol.

30. The mass defect of the nuclear reaction ${}_5\text{Be}^8 \rightarrow {}_4\text{Be}^8 + e^+$ is

- (A) $\Delta m = \text{At. mass of } {}_5\text{Be}^8 - \text{At. mass of } {}_4\text{Be}^8$
 (B) $\Delta m = \text{At. mass of } {}_5\text{Be}^8 - \text{At. mass of } {}_4\text{Be}^8 - \text{mass of one electron}$
 (C) $\Delta m = \text{At. mass of } {}_5\text{Be}^8 - \text{At. mass of } {}_4\text{Be}^8 + \text{mass of one electron}$
 (D) $\Delta m = \text{At. mass of } {}_5\text{Be}^8 - \text{At. mass of } {}_4\text{Be}^8 - \text{mass of two electrons}$

Sol.

Comprehension

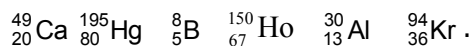
Mass defect in the nuclear reactions may be expressed in terms of the atomic masses of the parent and daughter nuclides in place of their nuclear masses.

29. The mass defect of nuclear reaction ${}_4\text{Be}^{10} \rightarrow {}_5\text{B}^{10} + e^-$ is

- (A) $\Delta m = \text{At. mass of } {}_4\text{Be}^{10} - \text{At. mass of } {}_5\text{Be}^{10}$
 (B) $\Delta m = \text{At. mass of } {}_4\text{Be}^{10} - \text{At. mass of } {}_5\text{Be}^{10} - \text{mass of one electron}$
 (C) $\Delta m = \text{At. mass of } {}_4\text{Be}^{10} - \text{At. mass of } {}_5\text{Be}^{10} + \text{mass of one electron}$
 (D) $\Delta m = \text{At. mass of } {}_4\text{Be}^{10} - \text{At. mass of } {}_5\text{Be}^{10} - \text{mass of one electron}$

EXERCISE – II**OBJECTIVE PROBLEMS (JEE ADVANCED)**

1. Classify each of the following nuclides as "beta emitter", or "positron emitter":



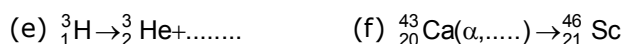
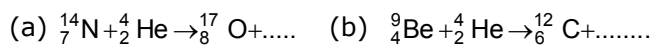
Note : ${}_{80}^{200}\text{Hg}$ and ${}_{67}^{165}\text{Ho}$ are stable.

Sol.

2. Of the three isobars ${}_{48}^{114}\text{Cd}$, ${}_{49}^{114}\text{In}$ and ${}_{50}^{114}\text{Sn}$, which is likely to be radioactive ? Explain your choice.

Sol.

3. Complete the following nuclear equations :

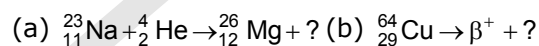


Sol.

4. What symbol is needed to complete the nuclear equation ${}_{29}^{63}\text{Cu}(p, \dots) \rightarrow {}_{29}^{62}\text{Cu}$?

Sol.

5. Complete the following equations.



Sol.

6. How many α and β particle will be emitted when a_cX changes to b_dY ?

Sol.

7. What is the α - activity in disintegration per minute 1 gm sample of ${}^{226}\text{Ra}$. ($t_{1/2} = 1620$ year)

Sol.

8. The half life of the nuclide Rn^{220} is 54.5 sec. What mass of radon is equivalent to 1 millicurie.

Sol.

9. The activity of the radioactive sample drops to $\left(\frac{1}{64}\right)^{\text{th}}$ of its original value in 2 hr find the decay constant (λ).

Sol.

10. ${}_{84}\text{Po}^{210}$ decays with α to ${}_{82}^{206}\text{Pb}$ with a half life of 138.4 days. If 1.0 gm of Po^{210} is placed in a closed tube, how much helium accumulate in 69.2 days at 1 atm & 273 K.

Sol.

11. The half life period of ${}_{53}\text{I}^{125}$ is 60 days. What % of radioactivity would be present after 240 days.

Sol.

12. At a certain instant a piece of radioactive material contains 10^{12} atoms. The half life of material is 30 days. Calculate the no. of disintegrations in one second.

Sol.

13. Calculate the age of a vegetarian beverage whose tritium content is only 15% of the level in living plants. Given $t_{1/2}$ for ${}_1\text{H}^3 = 12.3$ years.

Sol.

14. A radioactive substance decays 20% in 10 min if at start there are 5×10^{20} atoms present, after what time will the number of atoms be reduced to 10^{18} atoms ?

Sol.

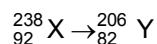
Fill in the blanks with appropriate items :

1. 1 Curie = _____ Bq.

2. ${}^{14}_6\text{C}$ decays by emission of _____.

3. Emission of a β - particle by a nuclide results in the formation _____ of the element.

4. The number of α and β - particles emitted, when the following nuclear transformation takes place are _____ and _____ respectively.



5. The nuclides with same difference of number of neutrons and number of protons are called _____.

6. When ${}^{30}_{15}\text{P}$ emits a positron, the daughter nuclide formed is _____.

7. A nuclide which lies above the zone of stability is likely to emit _____.

8. ${}^3_1\text{H}$ and ${}^4_2\text{He}$ are _____

EXERCISE – III**SUBJECTIVE PROBLEMS (JEE ADVANCED)**

1. Fallout from nuclear explosions contains ^{131}I and ^{90}Sr . Calculate the time required for the activity of each of these isotopes to fall to 1.0% of its initial value. Radioiodine and radiostrontium tend to concentrate in the thyroid and the bones, respectively, of mammals which ingest them. Which isotope is likely to produce the more serious long-term effects? Half-life of $^{131}\text{I} = 8$ days, $^{90}\text{Sr} = 19.9$ yrs

Sol.

2. $^{218}\text{Po}_{84}$ ($t_{1/2} = 3.05$ min) decay to $^{214}\text{Pb}_{82}$ ($t_{1/2} = 2.68$ min) by α -emission, while ^{214}Pb is a β -emitter. In an experiment starting with 1 gm atom of Pure ^{218}Po , how much time would be required for the number of nuclei of ^{214}Pb to reach maximum.

Sol.

3. Potassium having atomic mass = 39.1 u contains 93.10 mass % ^{39}K , having atomic mass 38.96371 u; 0.0118 mass % ^{40}K , which has mass of 40.0 u and is radioactive with $t_{1/2} = 1.3 \times 10^9$ y and 6.88 mass % ^{41}K having a mass of 40.96184 u. Calculate the specific activity of naturally occurring potassium.

Sol.

4. A mixture of ^{239}Pu and ^{240}Pu has a specific activity of 6×10^9 dis/s/g. The half lives of the isotopes are 2.44×10^4 y and 6.08×10^3 y respectively. Calculate the isotopic composition of this sample.

Sol.

5. In a nature decay chain series starts with $^{232}\text{Th}_{90}$ and finally terminates at $^{208}\text{Pb}_{82}$. A thorium ore sample was found to contain 8×10^{-5} ml of helium at 1 atm & 273 K and 5×10^{-7} gm of ^{232}Th . Find the age of ore sample assuming that source of He to be only due to decay of ^{232}Th . Also assume complete retention of helium within the ore. (Half-life of $^{232}\text{Th} = 1.39 \times 10^{10}$ Y)

Sol.

6. A sample of Uraninite, a Uranium containing mineral was found on analysis to contain 0.214 gm of Pb^{206} for every gram of Uranium. Assuming that the lead all resulted from the radioactive disintegration of the Uranium since the geological formation of the Uraninite and all isotopes of Uranium other than ^{238}U can be neglected. Estimate the day when the mineral was formed in the Earth's crust. $[t_{1/2} \text{ of } ^{238}\text{U} = 4.5 \times 10^9 \text{ years}]$.

Sol.

7. $^{92}_{92}\text{U}^{238}$ by successive radioactive decays changes to $^{82}_{82}\text{Pb}^{206}$. A sample of uranium ore was analyzed and found to contain 1.0 g of U^{238} and 0.1 g of Pb^{206} . Assuming that all the Pb^{206} had accumulated due to decay of U^{238} , find out the age of the ore. (Half life of $\text{U}^{238} = 4.5 \times 10^9$ years.)

Sol.

8. A sample pitch blende is found to contain 50% Uranium (U^{238}) and 2.425% Lead. Of this Lead only 93% was Pb^{206} isotope, if the disintegration constant is $1.52 \times 10^{-10} \text{ yr}^{-1}$. How old could be the pitch blende deposit.

Sol.

9. A 10 mL sample of a solution containing 1.0×10^{-7} Ci of ${}^3_1\text{H}$ is injected into the blood stream of a laboratory animal. After sufficient time for circulatory equilibrium to be established, 0.10 mL blood is found to have an activity of 20 dis/min. Calculate the blood volume of the animal.

Sol.

10. A sample of ${}^{131}_{53}\text{I}$, as iodine ion, was administered to a patient in a carrier consisting of 0.10 mg of stable iodide ion. After 4.00 days, 67.7% of the initial radioactivity was detected in the thyroid gland of the patient. What mass of the stable iodide ion had migrated to the thyroid gland? ($t_{1/2} = 8$ days.)

Sol.

EXERCISE – IV**PREVIOUS YEARS PROBLEMS****LEVEL – I****JEE MAIN**

1. In N_0 is the original mass of the substance of half-life period $t_{1/2} = 5$ years, then the amount of substance left after 15 years is –

[AIEEE-2002]

- (A) $\frac{N_0}{8}$ (B) $\frac{N_0}{16}$ (C) $\frac{N_0}{2}$ (D) $\frac{N_0}{4}$

Sol.

2. At a specific instant emission of radioactive compound is deflected in a magnetic field. The compound can emit –

[AIEEE-2002]

- (A) Electrons (B) Protons
(C) He^{2+} (D) Neutrons

Sol.

3. A radioactive sample at any instant has its disintegration rate 5000 disintegrations per minute. After 5 minutes, the rate is 1250 disintegrations per minute. Then, the decay constant (per minute) is –

[AIEEE-2003]

- (A) $0.2 \ln 2$ (B) $0.1 \ln 2$
(C) $0.8 \ln 2$ (D) $0.4 \ln 2$

Sol.

4. Which of the following cannot be emitted by radioactive substances during their decay ?

[AIEEE-2003]

- (A) Neutrinos (B) Helium nuclei
(C) Electrons (D) Protons

Sol.

5. Which of the following radiations has the least wavelength ?

[AIEEE-2003]

- (A) β -rays (B) α -rays
(C) X-rays (D) γ -rays

Sol.

6. When a U^{238} nucleus originally at rest, decay by emitting an alpha particle having a speed 'u' the recoil speed of the residual nucleus is –

[AIEEE-2003]

- (A) $-\frac{4u}{234}$ (B) $\frac{4u}{234}$
(C) $-\frac{4u}{238}$ (D) $\frac{4u}{238}$

Sol.

7. A nucleus with $Z = 92$ emits the following in a sequence : $\alpha, \beta^-, \beta^-, \alpha, \alpha, \alpha, \alpha, \alpha, \beta^-, \beta^-, \alpha, \beta^+, \beta^+, \alpha$. The Z of the resulting nucleus is –

[AIEEE-2003]

- (A) 78 (B) 82 (C) 74 (D) 76

Sol.

8. A nucleus disintegrates into two nuclear parts which have their velocities in the ratio of 2 : 1. The ratio of their nuclear sizes will be –

[AIEEE-2004]

- (A) $3^{1/2} : 1$ (B) $1 : 2^{1/3}$
(C) $2^{1/3} : 1$ (D) $1 : 3^{1/2}$

Sol.

9. The binding energy per nucleon of deuteron (${}^2_1\text{H}$) and helium nucleus (${}^4_2\text{He}$) is 1.1 MeV and 7 MeV respectively. If two deuteron nuclei react to form a single helium nucleus, then the energy released is–

[AIEEE-2004]

- (A) 23.6 MeV (B) 26.9 MeV
(C) 13.9 MeV (D) 19.2 MeV

Sol.

10. The intensity of gamma radiation from a given source is I . On passing through 36 mm of lead, it is reduced to $I/8$. The thickness of lead which will reduce the intensity to $I/2$ will be

[AIEEE-2005]

- (A) 6 mm (B) 9 mm
(C) 18 mm (D) 12 mm

Sol.

11. Starting with a sample of pure ${}^{66}\text{Cu}$, $7/8$ of it decays into Zn in 15 minutes. The corresponding half-life is

[AIEEE-2005]

- (A) 10 min (B) 15 min
(C) 5 min (D) $7\frac{1}{2}$ min

Sol.

12. If radius of the ${}_{13}^{27}\text{Al}$ nucleus is estimated to be 3.6 Fermi then the radius of ${}_{52}^{125}\text{Te}$ nucleus be nearly [AIEEE-2005]

(A) 6 fermi (B) 8 fermi
(C) 4 fermi (D) 5 fermi

Sol.

13. A nuclear transformation is denoted by $X(n, \alpha){}_3^7\text{Li}$. Which of the following is the nucleus of element of X ? [AIEEE-2005]

(A) ${}_{12}^{12}\text{C}_6$ (B) ${}_{10}^{10}\text{B}_5$
(C) ${}_{9}^9\text{B}_5$ (D) ${}_{11}^{11}\text{Be}_4$

Sol.

14. When ${}_3\text{Li}^7$ nuclei are bombarded by protons, and the resultant nuclei are ${}_4\text{Be}^8$, the emitted particles will be – [AIEEE 2006]

(A) gamma photons (B) neutrons
(C) alpha particles (D) beta particles

Sol.

15. An alpha nucleus of energy $\frac{1}{2}mv^2$ bombards a heavy nuclear target of charge Ze. Then the distance of closest approach for the alpha nucleus will be proportional to – [AIEEE 2006]

(A) $1/v^4$ (B) $1/Ze$
(C) v^2 (D) $1/m$

Sol.

16. If the binding energy per nucleon in ${}_3^7\text{Li}$ and ${}_2^4\text{He}$ nuclei are 5.60 MeV and 7.06 MeV respectively, then in the reaction $p + {}_3^7\text{Li} \rightarrow 2 {}_2^4\text{He}$ energy of proton must be – [AIEEE 2006]

(A) 1.46 MeV (B) 39.2 MeV
(C) 28.24 MeV (D) 17.28 MeV

Sol.

17. If M_0 is the mass of an oxygen isotope ${}_8\text{O}^{17}$, M_p and M_N are the masses of a proton and a neutron respectively, the nuclear binding energy of the isotope is [AIEEE-2007]

(A) $(M_0 - 8M_p) C^2$
(B) $(8M_p + 9M_N - M_0) C^2$
(C) $M_0 C^2$ (D) $(M_0 - 17 M_N) C^2$

Sol.

18. In gamma ray emission from a nucleus
[AIEEE-2007]
(A) both the neutron number and the proton number change
(B) there is no change in the proton number and the neutron number
(C) only the neutron number changes
(D) only the proton number changes

Sol.

19. The half-life period of a radio-active element X is same as the mean life time of another radio-active element Y. Initially they have the same number of atoms. Then
[AIEEE 2007]
(A) X will decay faster than Y
(B) Y will decay faster than X
(C) X and Y have same decay rate initially
(D) X and Y decay at same rate always

Sol.

20. This question contains Statement-1 and Statement-2. Of the four choices given after the statements, choose the one that best describes the two statements.

Statement-1 :

Energy is released when heavy nuclei undergo fission or light nuclei undergo fusion.

and

Statement-2 :

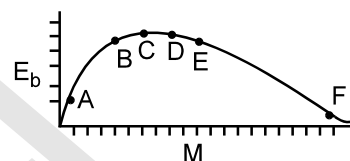
For heavy nuclei, binding energy per nucleon increases with increasing Z while for light nuclei it decreases with increasing Z.

[AIEEE-2008]

- (A) Statement-1 is true, Statement-2 is true; Statement-2 is a correct explanation for Statement-1
(B) Statement-1 is true, Statement-2 is true; Statement-2 is not a correct explanation for Statement-1
(C) Statement-1 is true, Statement-2 is false
(D) Statement-1 is false, Statement-2 is true

Sol.

21. The above is a plot of binding energy per nucleon E_b , against the nuclear mass M; A, B, C, D, E, F correspond to different nuclei. Consider four reactions :



- (i) $A + B \rightarrow C + \varepsilon$ (ii) $C \rightarrow A + B + \varepsilon$
(iii) $D + E \rightarrow F + \varepsilon$ and (iv) $F \rightarrow D + E + \varepsilon$
Where ε is the energy released ? In which reactions is ε positive.

[AIEEE - 2009]

- (A) (i) and (iv) (B) (i) and (iii)
(C) (ii) and (iv) (D) (ii) and (iii)

Sol.

LEVEL – II

JEE ADVANCED

1. If uranium (mass number 238 and atomic number 92) emits an α -particle, the product has mass no. and atomic no. [IIT -1981]

(A) 236 and 92 (B) 234 and 90
(C) 238 and 90 (D) 236 and 90

Sol.

2. Radioactive decay is a first order process. Radioactive carbon in wood sample decays with a half-life of 5770 years. What is the rate constant (in years^{-1}) for the decay? What fraction would remain after 11540 years? [IIT -1984]

Sol.

3. ${}_{90}^{234}\text{Th}$ disintegrates to give ${}_{82}^{206}\text{Pb}$ as the final product. How many alpha and beta particles are emitted during this process? [IIT -1986]

Sol.

4. Nuclear reactions accompanied with emission of neutron (s) are : [IIT -1988]

(A) ${}_{13}^{17}\text{Al} + {}_2^4\text{H} \rightarrow {}_{15}^{30}\text{P}$
(B) ${}_{6}^{12}\text{C} + {}_1^1\text{H} \rightarrow {}_7^{13}\text{N}$
(C) ${}_{15}^{30}\text{P} \rightarrow {}_{14}^{30}\text{S} + {}_1^0\text{e}$
(D) ${}_{96}^{241}\text{Am} + {}_2^4\text{He} \rightarrow {}_{97}^{244}\text{Bk} + {}_1^0\text{e}$

Sol.

5. An experiment requires minimum beta activity product at the rate of 346 beta particles per minute. The half life period of ${}_{42}^{99}\text{Mo}$, which is a beta emitter is 66.6 hours. Find the minimum amount ${}_{42}^{99}\text{Mo}$ required to carry out the experiment in 6.909 hours. [IIT -1989]

Sol.

6. In the nuclear process, ${}^{11}_6\text{C} \rightarrow {}^{11}_5\text{B} + \beta^+ + X$,
X stands for **[IIT - 1992]**
(A) neutrino (B) γ partical
(C) α particle (D) neutron

Sol.

7. Which of the following statement (s) is (are) correct ? **[IIT - 1994]**
(A) The rest mass of a stable nucleus is less than the sum of the rest masses of its separated nucleons.
(B) The rest mass of a stable nucleus is greater than the sum of the rest masses of its separated nucleons.
(C) In nuclear fusion, energy is released by fusing two nuclei of medium mass (ap proximately. 100 amu)
(D) None of these

Sol.

8. Fast neutrons can easily be slowed down by - **[IIT 1994]**
(A) The use of lead shielding
(B) Passing them through water
(C) Elastic collisions with heavy nuclei
(D) Applying a strong electric field

Sol.

9. Consider α particles, β particles and γ -rays, each having an energy of 0.5 MeV. In increasing order of penetrating powers, the radiations are - **[IIT- JEE, 1994]**
(A) α , β , γ (B) α , γ , β
(C) β , γ , α (D) γ , β , α

Sol.

10. One of the hazards of nuclear explosion is the generation of ${}^{90}\text{Sr}$ and its subsequent incorporation in bones. This nuclide has a half-life of 2.81 years. Suppose one microgram was absorbed by a new-born child, how much ${}^{90}\text{Sr}$ will remain in his bones after 20 years ?

[IIT -1995]

Sol.

11. Consider the following reaction : **[IIT 96]**
 ${}^2_1\text{H} + {}^2_1\text{H} = {}^4_2\text{He} + Q$
Mass of the deuterium atom = 2.0141 amu
Mass of helium atom = 4.0024 amu
This is a nuclear reaction in which the energy Q released is MeV
(A) Fusion, 24 (B) Fission, 24
(C) Fusion, 30 (D) Fission, 30

Sol.

12. Masses of two isobars ${}^{64}_{29}\text{Cu}$ and ${}^{64}_{30}\text{Zn}$ are 63.9298 amu and 63.9292 amu respectively. It can be concluded from these data that - **[IIT - 1997]**
(A) Both the isobars are stable
(B) Zn^{64} is radioactive, decaying to Cu^{64} through β -decay
(C) Cu^{64} is radioactive, decaying to Zn^{64} through γ -decay
(D) Cu^{64} is radioactive, decaying to Zn^{64} through β -decay

Sol.

13. Write a balanced equation for the reaction of ${}^{14}_7\text{N}$ with α -particle. **[IIT -1997]**

Sol.

14. Masses of two isobars ${}_{29}\text{Cu}^{64}$ and ${}_{30}\text{Zn}^{64}$ are 63.9298 amu and 63.9292 amu respectively. It can be concluded from these data that - [IIT - 1997]

- (A) Both the isobars are stable
 (B) Zn^{64} is radioactive, decaying to Cu^{64} through β -decay
 (C) Cu^{64} is radioactive, decaying to Zn^{64} through γ -decay
 (D) Cu^{64} is radioactive, decaying to Zn^{64} through β -decay

Sol.

15. The half-life of ${}^{131}\text{I}$ is 8 days. Given a sample of ${}^{131}\text{I}$ at time $t = 0$, we can assert that - [IIT - 1998]

- (A) No nucleus will decay before $t = 4$ days
 (B) No nucleus will decay before $t = 8$ days
 (C) All nuclei will decay before $t = 16$ days
 (D) A given nucleus may decay at any time after $t = 0$

Sol.

16. Let m_p be the mass of a proton, m_n the mass of neutron, M_1 the mass of a ${}_{10}\text{Ne}^{20}$ nucleus and M_2 the mass of a ${}_{20}\text{Ca}^{40}$ nucleus. Then [IIT 98]

- (A) $M_2 = 2M_1$ (B) $M_2 > 2M_1$
 *(C) $M_2 < 2M_1$ *(D) $M_1 < 10(m_n + m_p)$

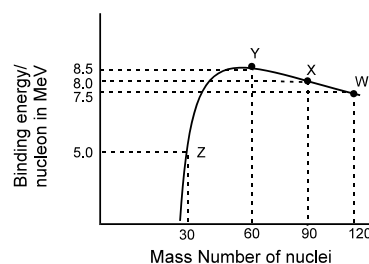
Sol.

17. Order of magnitude of density of Uranium nucleus is, [$m_p = 1.67 \times 10^{-27}$ kg] [IIT - 1999]

- (A) 10^{20} kg/m³ (B) 10^{17} kg/m³
 (C) 10^{14} kg/m³ (D) 10^{11} kg/m³

Sol.

18. Binding energy per nucleon versus mass number curve for nuclei is shown in the figure. W, X, Y and Z are four nuclei indicated on the curve. The process that would release energy is : [IIT - 1999]



- (A) $Y \rightarrow 2Z$ (B) $W \rightarrow X + Z$
 (C) $W \rightarrow 2Y$ (D) $X = Y + Z$

Sol.

19. Which of the following is a correct statement ? [IIT - 1999]

- (A) Beta rays are same as cathode rays
 (B) Gamma rays are high energy neutrons
 (C) Alpha particles are singly ionized helium atoms
 (D) Protons and neutrons have exactly the same mass

Sol.

20. ${}^{22}\text{Ne}$ nucleus, after absorbing energy, decays into two α -particles and an unknown nucleus. The unknown nucleus is - [IIT - 1999]

- (A) Nitrogen (B) Carbon
 (C) Boron (D) Oxygen

Sol.

21. The half-life period of a radioactive element X is same as the mean-life time of another radioactive element Y. Initially both of them have the same number of atoms. Then -
[IIT- 1999]

(A) X and Y have the same decay rate initially
(B) X and Y decay at the same rate always
(C) Y will decay at a faster rate than X
(D) X will decay at a faster rate than Y

Sol.

22. The number of neutrons accompanying the formation of $^{139}_{54}\text{Xe}$ and $^{94}_{38}\text{Sr}$ from the absorption of a slow neutron by $^{235}_{92}\text{U}$, followed by nuclear fission is ,
[IIT - 1999]
- (A) 0 (B) 2
(C) 1 (D) 3

Sol.

23. Two radioactive materials X_1 and X_2 have decay constants 10λ and λ respectively. If initially they have the same number of nuclei, then the ratio of the number of nuclei of X_1 and that of X_2 will be $1/e$ after a time -
[IIT- 2000]

(A) $1/(10\lambda)$ (B) $1/(11\lambda)$
(C) $11/(10\lambda)$ (D) $1/(9\lambda)$

Sol.

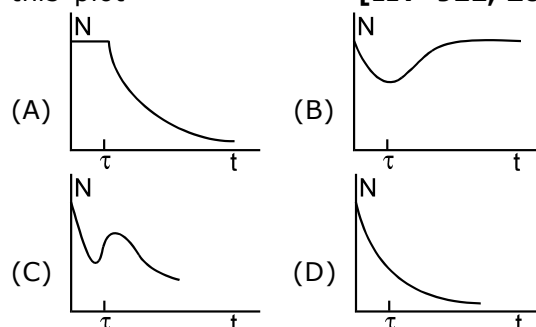
24. $^{238}_{92}\text{U}$ is radioactive and it emits α and β particles to form $^{206}_{82}\text{Pb}$. Calculate the number of α and β particles emitted in this conversion. An ore of $^{238}_{92}\text{U}$ is found to contain $^{238}_{92}\text{U}$ and $^{206}_{82}\text{Pb}$ in the weight ratio of 1 : 0.1. The half-life period of $^{238}_{92}\text{U}$ is 4.5×10^9 years. Calculate the age of the ore. [IIT - 2000]

Sol.

25. The electron emitted in beta radiation originates from -
[IIT- 2001]
- (A) inner orbits of atoms
(B) Free electrons existing in nuclei
(C) Decay of a neutron in a nucleus
(D) Photon escaping from the nucleus

Sol.

26. A radioactive sample consists of two distinct species having equal number of atoms initially. The mean life time of one species is τ and that of the other is 5τ . The decay products in both cases are stable. A plot is made of the total number of radioactive nuclei as a function of time. Which of the following figure best represents the form of this plot -
[IIT- JEE, 2001]



Sol.

27. The half-life of ^{215}At is $100\ \mu\text{s}$. The time taken for the radioactivity of a sample of ^{215}At to decay to $1/16^{\text{th}}$ of its initial value is - **[IIT - 2002]**
 (A) $400\ \mu\text{s}$ (B) $6.3\ \mu\text{s}$
 (C) $40\ \mu\text{s}$ (D) $300\ \mu\text{s}$

Sol.

28. Which of the following processes represents a gamma-decay - **[IIT - 2002]**
 (A) ${}^AX_Z + \gamma \rightarrow {}^AX_{Z-1} + a + b$
 (B) ${}^AX_Z + {}^1_0n \rightarrow {}^{A-3}X_{Z-2} + c$
 (C) ${}^AX_Z \rightarrow {}^AX_Z + f$
 (D) ${}^AX_Z + e_{-1} \rightarrow {}^AX_{Z-1} + g$

Sol.

29. ^{64}Cu (half-life = 12.8 h) decays by β^- emission (38%), β^+ emission (19%) and electron capture (43%). Write the decay products and calculate partial half-lives for each of the decay processes. **[IIT - 2002]**

Sol.

30. The nucleus of element X ($A = 220$) undergoes α -decay. If Q - value of the reaction is 5.5 MeV, then approximate kinetic energy of α -particle is : **[IIT - 2003]**
 (A) 5.6 MeV (B) 5.4 MeV
 (C) 4.9 MeV (D) 6.5 MeV

Sol.

31. ^{23}Na is the more stable isotope of Na. Find out the process by which $^{24}_{11}\text{Na}$ can undergo radioactive decay. **[IIT - 2003]**
 (A) β^- emission (B) α emission
 (C) β^+ emission (D) K electron capture

Sol.

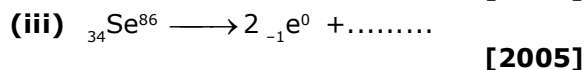
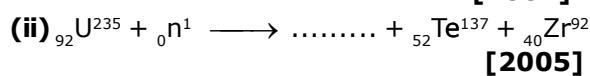
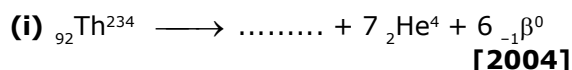
32. The volume and mass of a nucleus are related as **[IIT - 2003]**
 (A) $\propto m^3$ (B) $\propto \sqrt[3]{m}$
 (C) $\propto m$ (D) $\propto \frac{1}{m}$

Sol.

33. Activity of a radioactive substance after 280 days was 6000 d/s. It decreases to 3000 d/s after next 140 days. Its original activity was **[IIT - 2004]**
 (A) 12000 d/s (B) 9000 d/s
 (C) 20,000 d/s (D) 24000 d/s

Sol.

34. Complete and balance the following reactions.



Sol.

Sol.

37. Half life of a radioactive sample is 4 days. Find the probability that a particular nucleus of the radioactive material decays after 2 half life is
[IIT - 2006]

- (A) 1 (B) $\frac{1}{2}$
(C) $\frac{3}{2}$ (D) $\frac{3}{4}$

Sol.

35. In a star all Helium nuclei are converted into oxygen. If atomic mass of $M_{\text{He}} = 4.0026\text{U}$ and atomic mass of oxygen $M_{\text{O}} = 15.9994\text{U}$, then the reaction energy per atom of oxygen
[IIT - 2005]

- (A) 10.26 MeV (B) 0 MeV
(C) 5.24 MeV (D) 20.4 MeV

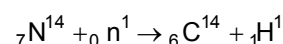
Sol.

36. **Column-I** **Column-II**
[IIT - 2006]

- | | |
|--|---|
| (A) Nuclear Fusion | (P) Some matter converted into energy |
| (B) Nuclear Fission occurs in nuclei | (Q) Generally having low atomic number |
| (C) β -decay | (R) Generally occurs in nuclei having higher atomic number. |
| (D) Exothermic reaction due to weak nuclear force. | (S) Essentially occurs |

Question No. 38 to 40 (3 questions)

Carbon 14 is used to determine the age of organic material. The procedure is based on the formation of ${}^{14}\text{C}$ by neutron capture in the upper atmosphere



${}^{14}\text{C}$ is absorbed by living organism during photosynthesis. The ${}^{14}\text{C}$ content is constant in living organism once the plant or animal dies, the uptake of carbon dioxide by it ceases and the level of ${}^{14}\text{C}$ in the dead being falls due to the decay which C^{14} undergoes.

${}_6\text{C}^{14} \rightarrow {}_7\text{N}^{14} + {}_{-1}\text{e}^0$ The half life period of ${}^{14}\text{C}$ is 5770 years. The decay constant (λ) can be

calculated by using the following formula $\lambda = \frac{0.693}{t_{1/2}}$

The comparison of the β^- activity of the dead matter with that of carbon still in circulation enables measurement of the period of the isolation of the material from the living cycle. The method however, ceases to be accurate over periods longer than 30,000 years. The proportion of ${}^{14}\text{C}$ to ${}^{12}\text{C}$ in living matter is 1 : 10^{12}
[JEE 2006]

38. Which of the following option is correct ?
(A) In living organisms, circulation of ${}^{14}\text{C}$ from atmosphere is high so the carbon content is constant in organism
(B) Carbon dating can be used to find out the age of earth crust and rocks
(C) Radioactive absorption due to cosmic radiation is equal to the rate of radioactive decay, hence the carbon content remains

constant in living organism
(D) Carbon dating cannot be used to determine concentration of ^{14}C in dead beings.

Sol.

- 39.** What should be the age of fossil for meaningful determination of its age ?
(A) 6 years (B) 6000 years
(C) 60000 years
(D) it can be used to calculate any age

Sol.

- 40.** A nuclear explosion has taken place leading to increase in concentration of C^{14} in nearby areas. C^{14} concentration is C_1 in nearby areas and C_2 in areas far away. If the age of the fossil is determined to be t_1 and t_2 at the places respectively, then

(A) The age of the fossil will increase at the place where explosion has taken place and

$$t_1 - t_2 = \frac{1}{\lambda} \ln \frac{C_1}{C_2}$$

(B) The age of the fossil will decrease at the place where explosion has taken place and

$$t_1 - t_2 = \frac{1}{\lambda} \ln \frac{C_1}{C_2}$$

(C) The age of fossil will be determined to be the same

$$(D) \frac{t_1}{t_2} = \frac{C_1}{C_2}$$

Sol.

- 41.** A positron is emitted from $^{23}_{11}\text{Na}$. The ratio of the atomic mass and atomic number of the resulting nuclide is **[JEE 2006]**

- (A) $\frac{22}{10}$ (B) $\frac{22}{11}$
(C) $\frac{23}{10}$ (D) $\frac{23}{12}$

Sol.

- 42.** In the options given below, let E denote the rest mass energy of a nucleus and n a neutron. The correct option is. **[IIT - 2007]**

$$(A) E(^{236}_{92}\text{U}) > E(^{137}_{53}\text{I}) + E(^{97}_{39}\text{Y}) + 2E(n)$$

$$(B) E(^{236}_{92}\text{U}) < E(^{137}_{53}\text{I}) + E(^{97}_{39}\text{Y}) + 2E(n)$$

$$(C) E(^{236}_{92}\text{U}) < E(^{140}_{56}\text{Ba}) + E(^{94}_{36}\text{Kr}) + 2E(n)$$

$$(D) E(^{236}_{92}\text{U}) = E(^{140}_{56}\text{Ba}) + E(^{94}_{36}\text{Kr}) + 2E(n)$$

Sol.

43. A positron is emitted from ${}_{11}^{23}\text{Na}$. The ratio of the atomic mass and atomic number of the resulting nuclide is. [IIT - 2007]

(A) 22/10 (B) 22/11
(C) 23/10 (D) 23/12

Sol.

44. A radio active sample S1 having an activity of $5\mu\text{Ci}$ has twice the number of nuclei as another sample S2 which has an activity of $10\mu\text{Ci}$. The half lives of S1 and S2 can be

[IIT-2008]

(A) 20 years and 5 years, respectively
(B) 20 years and 10 years, respectively
(C) 10 years each
(D) 5 years each

Sol.

45. **STATEMENT : 1** The plot of atomic number (γ -axis) versus number of neutrons (x -axis) for stable nuclei shows a curvature towards x -axis from the line of 45° slope as the atomic number is increased.

and

STATEMENT : 2 Proton-proton electrostatic repulsions begin to overcome attractive forces involving protons and neutrons in heavier nuclides.

[JEE 2008]

(A) STATEMENT -1 is True, STATEMENT-2 is True ; STATEMENT-2 is a correct explanation for STATEMENT-1

(B) STATEMENT-1 is True, STATEMENT-2 is True; STATEMENT-2 is NOT a correct explanation for STATEMENT-1

(C) STATEMENT-1 is True, STATEMENT-2 is False

(D) STATEMENT-1 is False, STATEMENT-2 is True

Sol.

46. The total number of α and β particles emitted in the nuclear reaction ${}_{92}^{238}\text{U} \longrightarrow {}_{82}^{214}\text{Pb}$ is

[IIT - 2009]

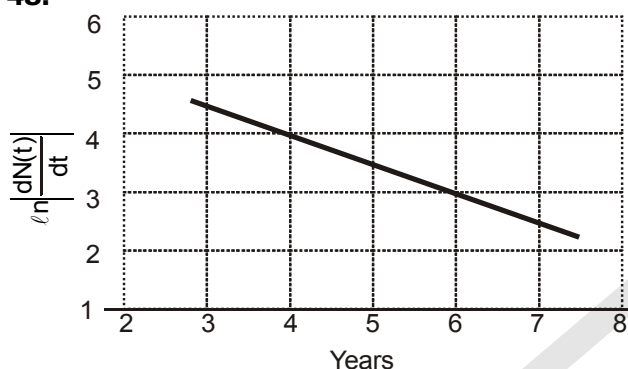
Sol.

47. The number of neutrons emitted when ${}_{92}^{235}\text{U}$ undergoes controlled nuclear fission to ${}_{54}^{142}\text{Xe}$ and ${}_{38}^{90}\text{Sr}$.

[IIT - 2010]

Sol.

48.

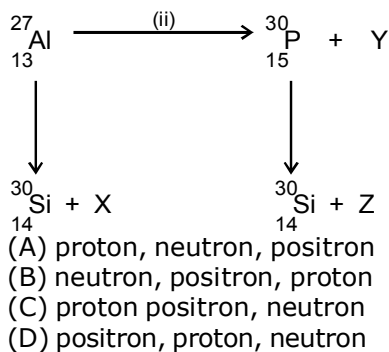


To determine the half life of a radioactive element, a student plots a graph of

$\ln \left| \frac{dN(t)}{dt} \right|$ versus t . Here $\frac{dN(t)}{dt}$ is the rate of radioactive decay at time t . If the number of radioactive nuclei of this element decreases by a factor of p after 4.16 years, the value of p is : **[2010, Physics]**

Sol.

49. Bombardment of aluminum by α -particle leads to its artificial disintegration in two ways, (i) and (ii) as shown. Products X, Y and Z respectively are,


[IIT - 2011]

Sol.

Paragraph for Question Nos. 50 to 51

The β -decay process, discovered around 1900, is basically the decay of a neutron (n). In the laboratory, a proton (p) and an electron (e^-) are observed as the decay products of the neutron. Therefore, considering the decay of a neutron as a two-body decay process, it was predicted theoretically that the kinetic energy of the electron should be a constant. But experimentally, it was observed that the electron kinetic energy has a continuous spectrum. Considering a three-body decay process, i.e. $n \rightarrow p + e^- + \bar{\nu}_e$, around 1930, Pauli explained the observed electron energy spectrum. Assuming the anti-neutrino ($\bar{\nu}_e$) to be massless and possessing negligible energy, and the neutron to be at rest, momentum and energy conservation principles are applied. From this calculation, the maximum kinetic energy of the electron is 0.8×10^6 eV. The kinetic energy carried by the proton is only the recoil energy. **[IIT - 2012]**

50. What is the maximum energy of the anti-neutrino?
 (A) Zero
 (B) Much less than 0.8×10^6 eV.
 (C) Nearly 0.8×10^6 eV.
 (D) Much larger than 0.8×10^6 eV.

Sol.

51. If the anti-neutrino had a mass of $3 \text{ eV}/c^2$ (where c is the speed of light) instead of zero mass, what should be the range of the kinetic energy, K , of the electron?

- (A) $0 \leq K \leq 0.8 \times 10^6 \text{ eV}$
 (B) $3.0 \text{ eV} \leq K \leq 0.8 \times 10^6 \text{ eV}$
 (C) $3.0 \text{ eV} \leq K < 0.8 \times 10^6 \text{ eV}$
 (D) $0 \leq K < 0.8 \times 10^6 \text{ eV}$

Sol.

52. Two radioactive nuclides A and B have half lives of 50 min and 10 min respectively. A fresh sample contains the nuclides of B to be eight times that of A. How much time should elapse so that the number of nuclides of A becomes double of B

- (A) 30 (B) 40
 (C) 50 (D) None

Sol.

53. Loss of a β^- particle is equivalent to
 (A) Increase of one proton only
 (B) Decrease of one neutron only
 (C) Both (A) and (B)
 (D) None of these

Sol.

54.

Column-I	Column-II
(A) Binding energy per nucleon increases in	(P) β -decay
(B) Mass number is conserved in	(Q) α -decay
(C) Atomic number is conserved in	(R) Nuclear fusion
(D) Mass of products formed is less than mass of reactants	(S) Nuclear fission

Sol.

55. A freshly prepared sample of a radioisotope of half-life 1386 s has activity 10^3 disintegrations per second. Given that $\ln 2 = 0.693$, the fraction of the initial number of nuclei (expressed in nearest integer percentage) that will decay in the first 80 s after preparation of the sample is **[IIT - 2013]**

Sol.

Paragraph for Question 56 and 57

The mass of nucleus A_ZX is less than the sum of the masses of (A-Z) number of neutrons and Z number of protons in the nucleus. The energy equivalent to the corresponding mass difference is known as the binding energy of the nucleus. A heavy nucleus of mass M can break into two light nuclei of masses m_1 and m_2 only if $(m_1 + m_2) < M$. Also two light nuclei of masses m_3 and m_4 can undergo complete fusion and form a heavy nucleus of mass M' only if $(m_3 + m_4) > M'$. The masses of some neutral atoms are given in the table below :

${}^1_1\text{H}$	1.007825 u	${}^2_1\text{H}$	2.014102 u	${}^3_1\text{H}$	3.016050 u	${}^4_2\text{He}$	4.002603 u
${}^6_3\text{Li}$	6.015123 u	${}^7_3\text{Li}$	7.016004 u	${}^{70}_{30}\text{Zn}$	69.925325 u	${}^{82}_{34}\text{Se}$	81.916709 u
${}^{152}_{64}\text{Gd}$	151.919803 u	${}^{206}_{82}\text{Pb}$	205.974455 u	${}^{209}_{83}\text{Bi}$	208.980388 u	${}^{210}_{84}\text{Po}$	209.982876 u

56. The correct statement is : **[IIT - 2013]**

- (A) The nucleus ${}^6_3\text{Li}$ can emit an alpha particle.
 (B) The nucleus ${}^{210}_{84}\text{Po}$ can emit a proton.
 (C) Deuteron and alpha particle can undergo complete fusion.
 (D) The nuclei ${}^{70}_{30}\text{Zn}$ and ${}^{82}_{34}\text{Se}$ can undergo complete fusion.

Sol.

57. The kinetic energy (in keV) of the alpha particle, when the nucleus ${}^{210}_{84}\text{Po}$ at rest undergoes alpha decay, is :

[IIT - 2013]

- (A) 5319 (B) 5422
 (C) 5707 (D) 5818

Sol.

58. Match List I of the nuclear processes with List II containing parent nucleus and one of the end products of each process and then select the correct answer using the codes given below the lists : **[IIT - 2013]**

List I

- (P) Alpha decay
 (Q) β^+ decay
 (R) Fission
 (S) Proton

List II

1. ${}^{15}_8\text{O} \rightarrow {}^{15}_7\text{N} + \dots$
 2. ${}^{238}_{92}\text{U} \rightarrow {}^{234}_{90}\text{Th} + \dots$
 3. ${}^{185}_{83}\text{Bi} \rightarrow {}^{184}_{82}\text{Pb} + \dots$
 4. ${}^{239}_{94}\text{Pu} \rightarrow {}^{140}_{57}\text{La} + \dots$

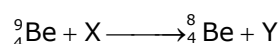
emission

Codes :

	P	Q	R	S
(A)	4	2	1	3
(B)	1	3	2	4
(C)	2	1	4	3
(D)	4	3	2	1

Sol.

59. In the nuclear transmutation



[IIT - 2013]

(X, Y) is (are)

- (A) (γ , n) (B) (p, D)
 (C) (n, D) (D) (γ , p)

Sol.

Answers

Answer Ex-I

OBJECTIVE PROBLEMS (JEE MAIN)

- | | | | | | | |
|---------|-------|-------|-------|-------|-------|-------|
| 1. B | 2. C | 3. A | 4. B | 5. B | 6. C | 7. A |
| 8. D | 9. A | 10. A | 11. C | 12. A | 13. D | 14. C |
| 15. ACD | 16. D | 17. C | 18. C | 19. C | 20. C | 21. B |
| 22. A | 23. B | 24. D | 25. A | 26. C | 27. C | 28. B |
| 29. A | 30. D | | | | | |

Answer Ex-II

OBJECTIVE PROBLEMS (JEE ADVANCED)

- beta emitter : ^{49}Ca , ^{30}Al , ^{94}Kr , positron emitter : ^{195}Hg , ^8B , ^{150}Ho
- $^{114}_{49}\text{In}$, odd number of nucleons
- (a) ^1_1H , (b) ^1_0n , (c) ^6_3Li , (d) $^0_{+1}\text{e}$, (e) $^0_{-1}\text{e}$, (f) p (proton)
- d, deuteron
- (a) ^1_1H (b) $^{64}_{28}\text{Ni}$ (c) $^0_{-1}\beta$ (d) ^1_0n
- $\alpha = \frac{a-b}{4}$; $\beta = d + \frac{(a-b)}{2} - c$
- 2.16×10^{12} events/min
- 1.06×10^{-15} kg
- $\lambda = 5.77 \times 10^{-4} \text{ sec}^{-1}$
- 32 ml
- 6.25 %
- 2.674×10^5 dps
- 33.67 years
- 4.65 hour

FILL IN THE BLANKS

- | | | | |
|-------------------------|--------------------------|------------------------|-------------|
| 1. 3.7×10^{10} | 2. β -rays | 3. isobar | 4. 8, 6 |
| 5. isodiaphers | 6. $^{30}_{14}\text{Si}$ | 7. β - particles | 8. isotones |

Answer Ex-III

SUBJECTIVE PROBLEMS (JEE ADVANCED)

- 53.1 days, 132 yrs, ^{90}Sr is likely to be serious, the iodine will soon be gone
- 4.125 min
- Specific activity = $30.69 \text{ dis. g}^{-1} \text{ s}^{-1}$
- $^{239}\text{Pu} = 45.1 \%$, $^{240}\text{Pu} = 54.9 \%$
- $t = 4.89 \times 10^9$ years
- 1.4×10^9 yrs
- 3.33×10^8 years
- $V = 1.1 \text{ L}$
- $t = 7.1 \times 10^8$ years
- 0.0958 mg

Answer Ex-IV**PREVIOUS YEARS PROBLEMS****LEVEL – I****JEE MAIN**

- | | | | | |
|-------|-------|-------|-------|-------|
| 1. A | 2. A | 3. D | 4. D | 5. B |
| 6. B | 7. A | 8. B | 9. A | 10. D |
| 11. C | 12. A | 13. B | 14. A | 15. D |
| 16. D | 17. B | 18. B | 19. B | 20. C |
| 21. A | | | | |

LEVEL – II**JEE ADVANCED**

- | | | | |
|---|---|-------------------------------------|---------|
| 1. B | 2. $1.2 \times 10^{-4} \text{ yrs}^{-1}, 1/4$ | 3. 7,6 | 4. A,D |
| 5. $3.451 \times 10^{-18} \text{ mol}$ | 6. A | 7. A | 8. B |
| 9. A | 10. $0.061 \mu\text{g}$ | 11. A | 12. D |
| 13. ${}_7\text{N}^{14} + {}_2\text{He}^4 \rightarrow {}_9\text{F}^{18}$ | 14. D | 15. D | 16. C,D |
| 17. B | 18. C | 19. A | 20. B |
| 22. D | 23. D | 24. $7.097 \times 10^8 \text{ yrs}$ | 25. C |
| 26. D | 27. A | 28. C | 29. |
| 31. A | 32. C | 33. D | 34. |
| 36. | 37. D | 38. C | 39. B |
| 41. C | 42. A | 43. C | 44. A |
| 45. A | 46. 8 | 47. 4 | 48. 8 |
| 50. C | 51. D | 52. C | 53. C |
| 54. $A \rightarrow P, Q, R, S$ $B \rightarrow P, Q, R, S$ $C \rightarrow P, Q, R, S$ $D \rightarrow P, Q, R, S$ | 55. 4 | | |
| 56. C | 57. A | 58. C | 59. AB |

THERMODYNAMICS

DEFINITION:

Thermodynamics deals with energy interaction b/w two bodies & its effect on the properties of matter.

Scope of thermodynamics:

- **Feasibility of a process**
- **Extent of a process**
- **Efficiency of a process**

TERMS USED IN THERMODYNAMICS

System + Boundary + Surrounding = Universe

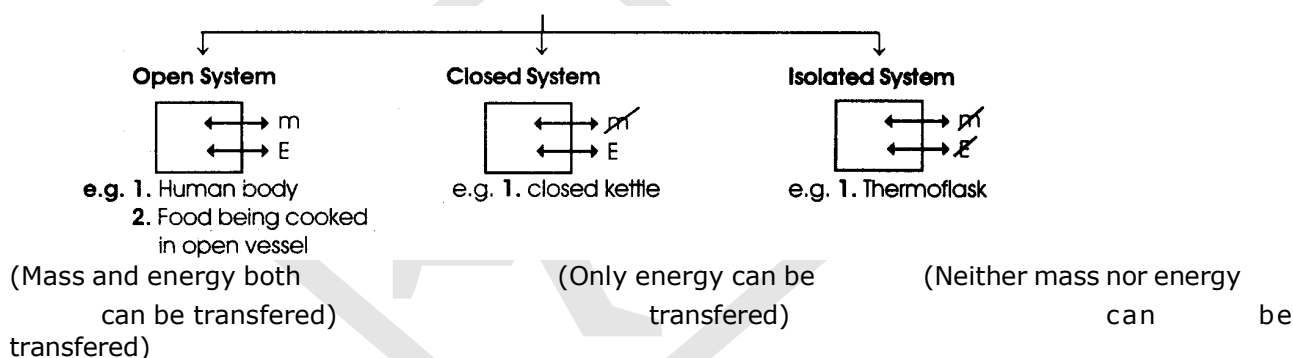
SYSTEM : The part of the universe under thermodynamical observation is called system.

SURROUNDINGS : All the part of the universe excepting system is called surroundings.

BOUNDARY : The part which separates system and surroundings is called boundary it may be rigid or flexible.

It may be diathermic (Heat can be exchanged) or adiabatic

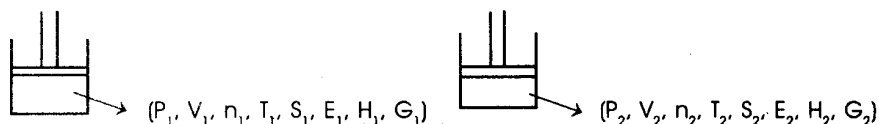
Types of Systems



STATE VARIABLES

State or condition of a system is described by certain measurable properties & these measurable properties are called state variables. e.g. mass, temperature, volume, pressure etc.

STATE FUNCTION



State function depends only on initial & final state of the system. It does not depend on the path or how process was carried out.

e.g. $\Delta U = \int_i^f du$ Where $\Delta U = u_f - u_i$

$$\int_i^f dT = \Delta T = T_f - T_i$$

Sol. The parameters which are required to completely define the state of the system are called **state functions**.

State functions are path independent function.

Process-I $\Rightarrow \Delta P = \Delta P \Leftarrow$ **Process - II**

$$\Delta V = \Delta V$$

$$\Delta n = \Delta n$$

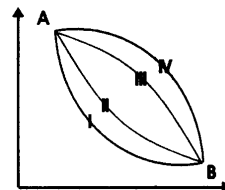
$$\Delta T = \Delta T$$

$$\Delta E = \Delta E$$

$$\Delta H = \Delta H$$

$$\Delta G = \Delta G$$

$$\Delta S = \Delta S$$



- Path independent means the difference in state functions will be same for any path followed between two states.

PHYSICAL PROPERTIES

EXTENSIVE PROPERTIES

1. These properties are dependent on mass
2. Example – V, n, G, H, E, S, etc.
3. additive in nature

INTENSIVE PROPERTIES

1. These properties are mass independent
2. Example – T, P, ρ , conc, μ (refractive, index), m.p., b.p., C_p , C_v , etc.
Specific heat, specific internal energy, coefficient of friction, viscosity, surface tension, vapour pressure, dielectric constant, P^H , emf of cell
3. Non additive in nature

PATH FUNCTION

Path function depends on the initial as well as final state of a system & also depends on the path of the process. e.g. heat and work.

CONDITION FOR A FUNCTION TO BE STATE FUNCTION

Euler's theorem $f = f(T, V)$. If f is a state function then

$$\frac{\partial}{\partial T} \left[\left(\frac{\partial f}{\partial V} \right)_T \right]_V = \frac{\partial}{\partial V} \left[\left(\frac{\partial f}{\partial T} \right)_V \right]_T$$

$$PV = nRT \quad \Rightarrow P = \frac{nRT}{V}$$

if pressure is a state function then

$$\frac{\partial}{\partial T} \left[\left(\frac{\partial P}{\partial V} \right)_T \right]_V = \frac{\partial}{\partial V} \left[\left(\frac{\partial P}{\partial T} \right)_V \right]_T \Rightarrow \left(\frac{\partial P}{\partial V} \right)_T = \frac{-nRT}{V^2} \Rightarrow \left(\frac{\partial P}{\partial T} \right)_V = \frac{nR}{V}$$

$$\frac{\partial}{\partial T} \left[\frac{-nRT}{V^2} \right]_V = \frac{-nR}{V^2} \Rightarrow \frac{\partial}{\partial V} \left[\left(\frac{\partial P}{\partial T} \right)_V \right]_T = \frac{-nR}{V^2}$$

Hence P is a state function.

e.g. $f(x, y) = ye^x + xy + x \ln y$

Show that $f(x, y)$ is a state function.

Sol. $\left(\frac{\partial f}{\partial x}\right)_y = ye^x + y + \ln y$ $\left(\frac{\partial f}{\partial y}\right)_x = e^x + x + x \cdot \frac{1}{y}$

$$\frac{\partial}{\partial x} \left[\left(\frac{\partial f}{\partial y} \right)_x \right]_y = \frac{\partial}{\partial x} [e^x + x + x/y]_y = e^x + 1 + \frac{1}{y}$$

$$\frac{\partial}{\partial y} \left[\left(\frac{\partial f}{\partial x} \right)_y \right]_x = \frac{\partial}{\partial y} [ye^x + y + \ln y]_x$$

$$= e^x + 1 + \frac{1}{y}$$

Hence $f(x, y)$ is a state function.

Two other important result from differential calculus will be used frequently.

Consider a function. $z = f(x, y)$. which can be rearranged $x = g(y, z)$ or $y = h(x, z)$

For example, $PV = nRT$, $P = \frac{nRT}{V}$, $T = \frac{PV}{nR}$

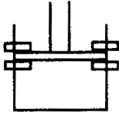
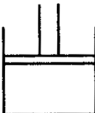
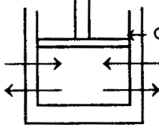
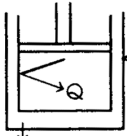
in this case

$$\left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z}$$

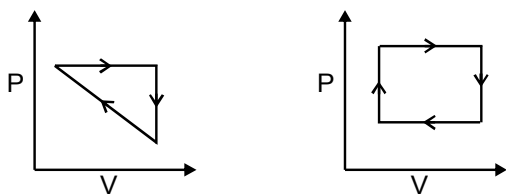
The cyclic rule will also be used.

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

THERMODYNAMIC PROCESSES

	PROCESS	SPECIAL CONDITION	CONSTRAINTS
(1).	Isochoric process	$V = \text{constant}$, $\Delta V = 0$	 Piston is not allowed to move
(2).	Isobaric process	$P = \text{constant}$, $\Delta P = 0$	 Piston is free to move
(3).	Isothermal process	$T = \text{constant}$, $\Delta T = 0$	 diathermal wall
(4).	Adiabatic process	$Q = \text{neither enters nor leaves the system}$	 Adiabatic wall

(5) Cyclic Process: System undergoes series of changes & ultimately comes back to initial state.



REVERSIBLE & IRREVERSIBLE PROCESS

(1) Quasi-Static(Reversible)Process: If system & surrounding can restore their original state by reversing the direction of the process then process is called reversible process. In reversible process, there is no loss of energy.

These are slow process as it takes infinite time. System & surrounding are always in equilibrium. Reversible process is a theoretical process. Reversible process is most efficient with respect to work.

In reversible process $P_{\text{ext}} = P_{\text{int}}$

If all the above criteria are not fulfilled by any process, then it is known as irreversible process.

* irreversible process is a fast process. It takes definite time for completion

* **In irreversible process $P_{\text{ext}} \neq P_{\text{int}}$**

*It is an actual process. It is carried out in multiple stages and it tends towards reversible process.



HEAT AND WORK

Heat & work both are forms of energy. Both are boundary phenomena and take place at the interface of the system & surroundings.

Work ———— Mechanical work $\Rightarrow F \cdot d$
 Electrical work $\Rightarrow v i t$
 Gravitational work $\Rightarrow mgh$

SIGN CONVENTION OF HEAT & WORKDONE

Expansion \longrightarrow **$W \Rightarrow -ve$**

Compression \Rightarrow **$W \Rightarrow +ve$**

Heat given to the system $\Rightarrow +ve$

Heat loss (it released) $\Rightarrow -ve$

Types of equilibrium

- (1) Thermal equilibrium \longrightarrow Equality of temperature
- (2) Mechanical equilibrium \longrightarrow Equality of pressure
- (3) Material equilibrium \Rightarrow no. of moles constant

When all the three equilibrium are established in a system, system is in true thermodynamics equilibrium

TOTAL ENERGY & INTERNAL ENERGY

Total energy = $\underset{\substack{\downarrow \\ \text{due to motion} \\ \text{of the body}}}{\text{KE}} + \underset{\substack{\downarrow \\ \text{due to presence} \\ \text{of electric \& magnetic Field}}}{\text{PE}} + \text{IE}$

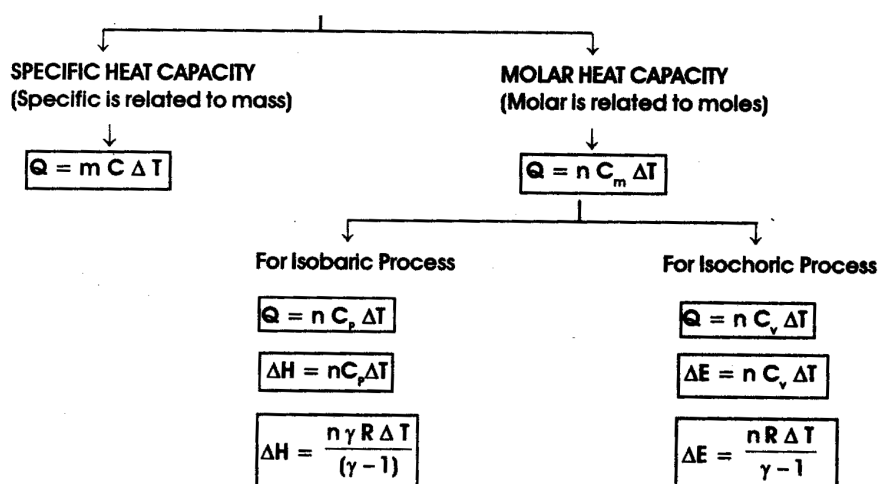
If system is at rest & no external electric & magnetic field is present then

$$E = U$$

Internal energy : Internal energy of gaseous molecule present in a system or body is equal to sum of all possible kinds of energy.

Energy $U = \text{TE} + \text{RE} + \text{VE} + \text{Chemical energy} + \text{nuclear energy} + \text{electron spin energy} + \text{PE}$

HEAT CAPACITIES



For ideal gas

- $C_p - C_v = R \quad \Rightarrow \quad C_p = \left(\frac{\gamma R}{\gamma - 1} \right) = (f/2 + 1) R \quad f \rightarrow \text{degree of freedom}$
- $C_p/C_v = \gamma \quad \Rightarrow \quad C_v = \frac{R}{(\gamma - 1)} = f/2 R \quad \gamma \rightarrow \text{Poisson's Ratio}$

	n_{tr}	n_{R_0}	n_{vib}	C_v		C_p		γ	
				Excl. Vib	Incl. Vib	Excl. Vib	Incl. Vib	Excl. Vib	Incl. Vib
Mono	3	0	0	$\frac{3}{2}R$	$\frac{3}{2}R$	$\frac{5}{2}R$	$\frac{5}{2}R$	$\frac{5}{3}$	$\frac{5}{3}$
Di	3	2	1	$\frac{5}{2}R$	$\frac{7}{2}R$	$\frac{7}{2}R$	$\frac{9}{2}R$	$\frac{7}{5}$	$\frac{9}{7}$
Tri \nearrow Linear \searrow NonLinear	3	2	4	$\frac{5}{2}R$	$\frac{13}{2}R$	$\frac{7}{2}R$	$\frac{15}{2}R$	$\frac{7}{5}$	$\frac{15}{13}$
	3	3	3	$3R$	$6R$	$4R$	$7R$	$\frac{4}{3}$	$\frac{7}{6}$

• **For Isobaric Process :**

$$Q = nC_p\Delta T \quad \text{and} \quad Q = \Delta H$$

$$\Delta H = nC_p\Delta T = \frac{n\gamma R\Delta T}{(\gamma - 1)}$$

For isochoric process

$$Q = nC_v\Delta T \quad \text{and} \quad Q = \Delta E$$

$$\Delta E = nC_v\Delta T = \frac{nR\Delta T}{\gamma - 1}$$

For liquid and solids

$$C_p \approx C_v$$

$$U = \frac{f}{2}nRT$$

$$\Delta U = \frac{f}{2}RT\Delta n_g$$

$$\Delta n_g C_v T = \frac{f}{2}RT\Delta n_g$$

$$C_v = \frac{f}{2}R$$

Total degree of freedom = $3n$

where n = no of atoms

for vibrational $u = f nRT$

$$C_{v_{\text{vibrational}}} = f_{\text{vibrational}} \cdot R$$

$$\text{Total } C_v = \left(\frac{f_{\text{trans}}}{2} + \frac{f_{\text{rotate}}}{2} + f_{\text{vibrational}} \right) \cdot R$$

LAW OF THERMODYNAMICS

(1) ZEROth LAW

Based on thermal equilibrium if A & B, & B & C are in thermal equilibrium then A & C must be in thermal equilibrium.

(2) FIRST LAW OF THERMODYNAMICS

First law of thermodynamics is based on energy conservation

$$\begin{aligned} E_2 &= E_1 + q + w & (E_1 \text{ is the } E_i) \\ E_2 - E_1 &= q + w & (E_1 + q + w \text{ is } E_f) \\ & & (E_i = E_f) \end{aligned}$$

$$\Delta E = q + w$$

or $\Delta U = q + w$

For an isolated system, $q = 0$, $w = 0$

$$\Delta U = 0$$

or $U = \text{constant}$

For cyclic process.

$$\oint du = 0$$

$$\Rightarrow \oint (dq + dw) = 0$$

$$\Rightarrow \boxed{q + w = 0}$$

Work done = $-F_{\text{ext}} \cdot dx$

$$= -P \cdot A \cdot dx$$

$$\boxed{dW = -P_{\text{ext}} dV}$$

for expansion $\rightarrow dW = -ve$

compression $\rightarrow dW = +ve$

$$dq = CdT \Rightarrow dq_v = C_v dT$$

$$C_v = \frac{dq_v}{dT} = \frac{q_v}{\Delta T}$$

For an isochoric process $dv = 0$

$$dU = q_v \Rightarrow \boxed{dU = C_v dT}$$

$$dU = n C_v dT$$

$$\boxed{\Delta U = n C_v (T_2 - T_1)}$$

If C_v is a function of temperature

$$\Delta U = n \int_{T_1}^{T_2} C_v dT$$

We know that

$$U = f(T, V, P)$$

consider

$$U = f(T, V)$$

$$du = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV$$

For isochoric process $dv = 0$

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT$$

for 1 mole of gas

$$C_v dT = \left(\frac{\partial U}{\partial T} \right)_V dT$$

$$C_v = \left(\frac{\partial U}{\partial T} \right)_V \Rightarrow \boxed{du = C_v dT}$$

For an ideal gas $U = f(T)$ only

$$\left(\frac{\partial U}{\partial V} \right)_T = 0$$

$$du = C_v dT$$

$$\Delta U = n C_v \Delta T = n C_v (T_2 - T_1)$$

$$\boxed{\Delta U = n C_v \Delta T = n C_v (T_2 - T_1)}$$

ENTHALPY

$$\begin{aligned}
 - \quad H &= U + PV \\
 dH &= dU + d(PV) \\
 \int dH &= \int dU + P \int dV
 \end{aligned}$$

at constant pressure

$$\Rightarrow \Delta H = \Delta U + P\Delta V$$

From, 1st law of thermodynamics at constant pressure.

$$\begin{aligned}
 dU &= dq_p + dW \\
 dU &= dq_p - PdV \\
 dq_p &= dU + PdV \\
 dH &= dU + PdV \\
 \Delta H &= \Delta U + P\Delta V \quad \dots\dots\dots(1)
 \end{aligned}$$

at constant volume

$$\Delta H = \Delta U + V\Delta P \quad \dots\dots\dots(2)$$

When P & V both changes

$$\begin{aligned}
 \Delta H &= \Delta U + (P_2V_2 - P_1V_1) \quad \dots\dots\dots(3) \\
 \Delta H &= \Delta U + d(PV) \\
 \Delta H &= \Delta U + d(nRT) \\
 \Delta H &= \Delta U + RT\Delta n_g
 \end{aligned}$$

For an ideal gas expansion or compression

$$\begin{aligned}
 \Delta H &= \Delta U + nR\Delta T \\
 \Delta H &= nC_v\Delta T + nR\Delta T \\
 &= n\Delta T[C_v + R] \\
 \Delta H &= n\Delta T C_p
 \end{aligned}$$

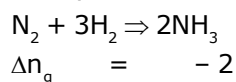
We know that, $H = f(T, P)$

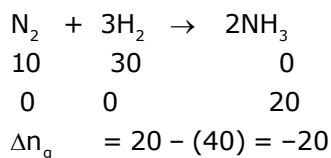
$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$$

At constant pressure

$$\begin{aligned}
 dP &= 0 \\
 dH &= \left(\frac{\partial H}{\partial T}\right)_P dT \\
 C_p &= \left(\frac{\partial H}{\partial T}\right)_P
 \end{aligned}$$

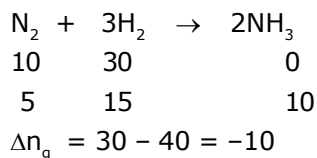
**Calculation of Δn_g for any chemical reaction:





$$\Delta n_g = n_{g(f)} - n_{g(i)}$$

If reaction is 50% completed.



WORKDONE CALCULATION

(1) Isochoric process:

$$V = \text{constant}$$

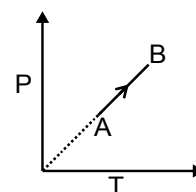
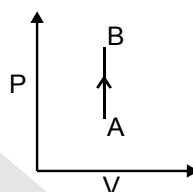
$$dV = 0$$

$$W = 0$$

$$dU = dq_v$$

$$\Delta U = q_v = nC_v\Delta T$$

$$\Delta H = nC_p\Delta T$$



(2) Isobaric process:

$$W = -P_{\text{ext}}(V_2 - V_1)$$

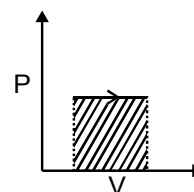
Reversible & isobaric process

$$W = -P(V_2 - V_1)$$

$$= -nR(T_2 - T_1)$$

Irreversible & isobaric process

$$P_1 = P_2 = P_{\text{ext}}$$



For reversible & irreversible isobaric or isochoric process, workdone is same.

3. Isothermal process.

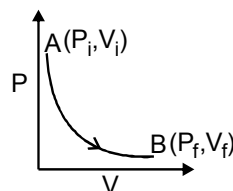
(a) Reversible Expansion or compression

$$W = -P \int dv$$

$$= -\int P_{\text{gas}} dV$$

$$= -\int \frac{nRT}{V} dV$$

$$\Rightarrow W = -nRT \ln \frac{V_f}{V_i}$$



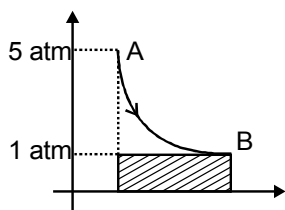
$$W = -nRT \ln \frac{P_i}{P_f}$$

In Expansion $W = -ve$

$$\Delta E = 0$$

$$q = -W$$

(b) Single stage irreversible expansion



$$W = -P_{\text{ext}}(V_2 - V_1)$$

$$|W_{\text{rev}}| > |W_{\text{irr}}| \text{ (in case of expansion)}$$

$$W = -P_{\text{ext}} \left[\frac{nRT}{P_2} - \frac{nRT}{P_1} \right]$$

$$W = -nRT P_{\text{ext}} \left[\frac{1}{P_2} - \frac{1}{P_1} \right]$$

(c) Two Stage irreversible Expansion:

Stage I.

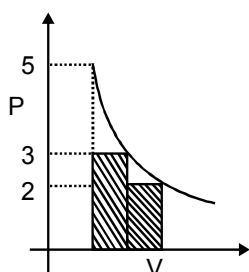
$$P'_{\text{ext}} = 3 \text{ atm}$$

$$P_i = 5 \text{ atm}$$

Stage II.

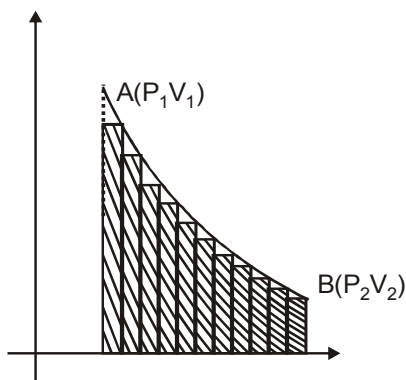
$$P''_{\text{ext}} = 2 \text{ atm}$$

$$P_f = 2 \text{ atm}$$



Workdone in 2nd stage > Workdone in 1st stage

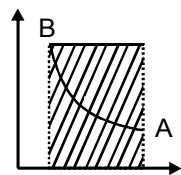
(d) n- stage expansion



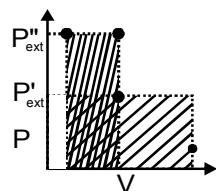
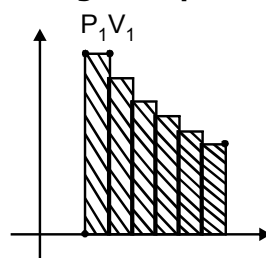
Compression - (One stage Compression)

$$|W_{\text{irr}}| = P_{\text{ext}} \Delta V$$

$$P_1 = 1 \text{ atm}, P_2 = 5 \text{ atm}, P_{\text{ext}} = 5 \text{ atm}$$



$$|W_{\text{irr}}| > |W_{\text{rev}}| \quad \text{For compression}$$

Two stage Comp.**n stage Comp**

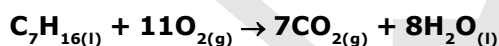
Ex.1 2 moles of an ideal gas initially present in a piston fitted cylinder at 300 K, and 10 atm are allowed to expand against 1 atm but the piston was stopped before it established the mechanical equilibrium. If temperature were maintained constant through out the change and system delivers 748.26 J of work, determine the final gas pressure and describe the process on PV diagram.

Sol. $W_{\text{irr}} = -748.26$

$$W_{\text{irr}} = -P_{\text{ext}} \left[\frac{1}{P_2} - \frac{1}{P_1} \right] nRT$$

$$P_2 = 4 \text{ atm}$$

Ex.2 1150 Kcal heat is released when following reaction is carried out at constant volume.



Find the heat change at constant pressure.

The pressure of liquid is a linear function of volume ($P = a + bV$) and the internal energy of the liquid is $U = 34 + 3PV$ find $a, b, w, \Delta E$ & ΔH for change in state from 100 Pa, 3m³ to 400 Pa, 6m³

Sol. $100 = a + bV$

$$\Rightarrow 100 = a + 3b$$

Also, $400 = a + 6b$

$$\Rightarrow \begin{aligned} a &= -200 \\ b &= 100 \end{aligned}$$

$$\begin{aligned} \Delta U &= 34 + 3(P_2V_2 - P_1V_1) \\ &= 6300 \text{ J} \end{aligned}$$

$$\begin{aligned} \Delta H &= \Delta U + P_2V_2 - P_1V_1 \\ &= 6300 + 2100 = 8400 \text{ J} \end{aligned}$$

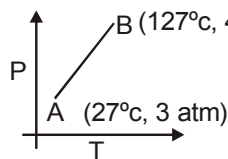
P is a linear function

$$P_{\text{ext}} = \frac{400 + 100}{2} = 250$$

$$\begin{aligned} W &= -P_{\text{ext}}(dV) \\ &= -250(6 - 3) = -750 \text{ J} \end{aligned}$$

Ex.3 4 moles of an ideal gas ($C_v = 15 \text{ J}$) is subjected to the following process represented on $P - T$ graph. From the given data find out whether the process is isochoric or not? also calculate q , w , ΔU , ΔH ,

Sol.



$$PV = nRT$$

$$4V = 4R \times 400$$

$$V = 400 R \quad \dots\dots\dots(1)$$

$$3V = 4R \times 300$$

$$V = 400 R \quad \dots\dots\dots(2)$$

i.e., V is constant

$$w = 0$$

$$\Delta U = nC_v \Delta T \Rightarrow 4 \times 15 \times 100 = 6000 \text{ J}$$

$$\Delta H = nC_p \Delta T \Rightarrow n(C_v + R) \Delta T$$

$$\Rightarrow 4 \times (15 + 8.3) \times 100$$

$$\Rightarrow 9320 \text{ J}$$

$$q = \Delta U = 6 \text{ kJ}$$

Ex.4 2 mole of a gas at 1 bar and 300 K are compressed at constant temperature by use of a constant pressure of 5 bar. How much work is done on the gas?

Sol. $w = -nRT \times P_{\text{ext}} \left[\frac{1}{P_2} - \frac{1}{P_1} \right]$
 $= 19953.6 \text{ J}$

Ex.5 2 moles of an ideal diatomic gas ($C_v = 5/2 R$) at 300 K, 5 atm expanded irreversibly and adiabatically to a final pressure of 2 atm against a constant pressure of 1 atm.

(1) Calculate final temperature q , w , ΔH & ΔU

(2) Calculate corresponding values if the above process is carried out reversibly.

Sol.. $w = C_v(T_2 - T_1) = -P_{\text{ext}} R \left[\frac{T_2}{P_2} - \frac{T_1}{P_1} \right]$

Given $T_2 = 270 \text{ K}$

$$P_{\text{ext}} = 1, P_2 = 2, P_1 = 5$$

$$q = 0$$

$$w = \Delta U = nC_v \Delta T$$

$$= -1247.1 \text{ J}$$

$$\Delta H = nC_p \Delta T$$

$$= 1745.94 \text{ J}$$

If process is reversible

$$Pv^\gamma = \text{Constant}$$

$$P^{1-\gamma} T^\gamma = \text{Constant}$$

$$T = 231 \text{ K}$$

ADIABATIC IDEAL GAS EXPANSION & COMPRESSION

$$dq = 0$$

$$dU = dW \Rightarrow \Delta U = W$$

$$W = nC_V \Delta T = nC_V (T_2 - T_1)$$

For an ideal gas $C_p - C_v = R$

$$C_V = \frac{R}{\gamma - 1}$$

REVERSIBLE ADIABATIC EXPANSION OR COMPRESSION

$$nC_V dT = -P_{\text{ext}} dV$$

$$P_{\text{int}} = dP = P_{\text{ext}}$$

$$P_{\text{int}} = P_{\text{gas}} = \frac{nRT}{V}$$

$$\int nC_V dT = - \int \frac{nRT}{V} dV$$

$$C_V \int \frac{dT}{T} = -R \int \frac{dV}{V}$$

$$C_V \ln \frac{T_2}{T_1} = -R \ln \frac{V_2}{V_1}$$

$$\frac{R}{\gamma - 1} \ln \frac{T_2}{T_1} = -R \ln \frac{V_2}{V_1} \Rightarrow \frac{1}{\gamma - 1} \ln \frac{T_2}{T_1} = -\ln \frac{V_2}{V_1}$$

$$\ln \frac{T_2}{T_1} = -(\gamma - 1) \ln \frac{V_2}{V_1} \Rightarrow \ln \frac{T_2}{T_1} = \ln \left(\frac{V_1}{V_2} \right)^{\gamma - 1}$$

$$\Rightarrow \frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{\gamma - 1}$$

$$\Rightarrow T_2 (V_2)^{\gamma - 1} = V_1^{\gamma - 1} T_1$$

$$TV^{\gamma - 1} = \text{Constant}$$

$$\frac{PV}{nR} V^{\gamma - 1} = \text{Constant}$$

$$\Rightarrow PV^{\gamma} = \text{Constant}$$

IRREVERSIBLE ADIABATIC COMPRESSION & EXPANSION

$$\begin{aligned}
 dU &= dW \\
 \Rightarrow nC_V(T_2 - T_1) &= -P_{\text{ext}} dV \\
 nC_V(T_2 - T_1) &= -P_{\text{ext}} [V_2 - V_1] \\
 nC_V(T_2 - T_1) &= -P_{\text{ext}} \left[\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right] \\
 &= -P_{\text{ext}} nR \left[\frac{T_2}{P_2} - \frac{T_1}{P_1} \right]
 \end{aligned}$$

$$C_V(T_2 - T_1) = -P_{\text{ext}} R \left[\frac{T_2}{P_2} - \frac{T_1}{P_1} \right]$$

COMPARISON OF REVERSIBLE ISOTHERMAL & REVERSIBLE ADIABATIC IDEAL GAS EXPANSION.

- (1) If final volumes are same.

Isothermal process.

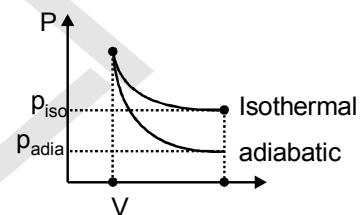
$$\begin{aligned}
 P_1 V_1 &= P_{\text{iso}} V_2 \\
 \Rightarrow \frac{V_2}{V_1} &= \frac{P_1}{P_{\text{iso}}}
 \end{aligned}$$

Adiabatic process.

$$\begin{aligned}
 P_1 V_1^\gamma &= P_{\text{adia}} V_2^\gamma \\
 \Rightarrow \left(\frac{V_2}{V_1} \right)^\gamma &= \frac{P_1}{P_{\text{adia}}}
 \end{aligned}$$

$$\frac{V_2}{V_1} > 1 \Rightarrow \left(\frac{V_2}{V_1} \right)^\gamma > \frac{V_2}{V_1} \Rightarrow \frac{P_1}{P_{\text{adia}}} > \frac{P_1}{P_{\text{iso}}}$$

$$\Rightarrow P_{\text{iso}} > P_{\text{adia}}$$



- (2) If final pressures are same

Isothermal process.

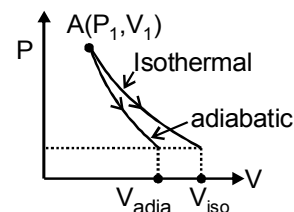
$$\begin{aligned}
 P_1 V_1 &= P_2 V_{\text{iso}} \\
 \frac{V_1}{V_{\text{iso}}} &= \frac{P_2}{P_1} \quad \dots\dots(1)
 \end{aligned}$$

$$P_1 V_1^\gamma = P_2 V_{\text{adia}}^\gamma$$

$$\frac{V_1}{V_{\text{adia}}} = \left(\frac{P_2}{P_1} \right)^{1/\gamma}$$

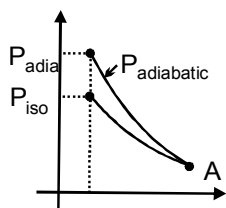
in ideal gas expansion, $|W_{\text{iso}}| > |W_{\text{adia}}|$

$$\text{Hence } \Rightarrow V_{\text{iso}} > V_{\text{adia}}$$



Compression

- (1) If final volumes are same



For isothermal process

$$P_1 V_1 = P_{iso} V_2$$

$$\frac{V_1}{V_2} = \frac{P_{iso}}{P_1} \quad \dots\dots\dots(1)$$

Adiabatic process.

$$P_1 V_1^\gamma = P_{adia} V_2^\gamma$$

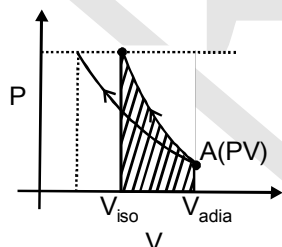
$$\left(\frac{V_1}{V_2}\right)^\gamma = \frac{P_{adia}}{P_1} \quad \dots\dots\dots(2)$$

$$\Rightarrow \left(\frac{V_1}{V_2}\right)^\gamma = \frac{V_1}{V_2}$$

$$\Rightarrow \frac{P_{adia}}{P_1} > \frac{P_{iso}}{P_1}$$

$$\boxed{P_{adia} > P_{iso}}$$

- (2) If final pressures are same



$$P_1 V_1 = P_2 V_{iso} \quad \dots\dots\dots(1)$$

$$P_1 V_1^\gamma = P_2 V_{adia}^\gamma \quad \dots\dots\dots(2)$$

$$\left(\frac{V_1}{V_{adia}}\right)^\gamma = \frac{P_2}{P_1} \Rightarrow \frac{V_{adia}}{V_1} = \left(\frac{P_1}{P_2}\right)^{1/\gamma}$$

$$\Rightarrow \frac{V_1}{V_{adia}} = \left(\frac{P_2}{P_1}\right)^{1/\gamma} < \frac{P_2}{P_1}$$

$$\frac{V_1}{V_{adia}} < \frac{V_1}{V_{iso}}$$

$$\Rightarrow \boxed{V_{adia} > V_{iso}}$$

POLYTROPIC PROCESS

$$PV^x = \text{Const}$$

$$W = - \int P_{\text{ext}} dV$$

$$= - \int P_{\text{gas}} dV$$

$$= -k \int_{V_1}^{V_2} V^{-x} dV \Rightarrow w = \frac{-k}{-x+1} [V_2^{-x+1} - V_1^{-x+1}]$$

$$= \frac{-1}{-x+1} [V_2 k V_2^{-x} - V_1 k V_1^{-x}]$$

$$W = \frac{1}{x-1} [P_2 V_2 - P_1 V_1]$$

MOLAR HEAT CAPACITY OF POLYTROPIC PROCESS

$$dU = dq + dW$$

$$nC_v dT = nC_m dT + (-PdV)$$

$$C_m = C_v + \frac{PdV}{ndT} \quad \dots\dots\dots(1)$$

$$PV = nRT$$

$$kV^{-x} V = nRT$$

$$kV^{-x+1} = nRT$$

$$k(-x+1)V^{-x} \frac{dV}{dT} = nR$$

$$\frac{dV}{dT} = \frac{nR}{k(1-x)V^{-x}} = \frac{nR}{(1-x)P}$$

$$C_m = C_v + \frac{p}{n} \frac{nR}{(1-x)P}$$

$$\Rightarrow \boxed{C_v + \frac{R}{1-x} = C} \quad x \neq 1$$

LIMITATIONS OF FIRST LAW OF THERMODYNAMICS

1. First law of thermodynamics does not give information regarding the direction of propagation of a process
2. First law of thermodynamics does not tell us why an equilibrium is attained.
3. First law of thermodynamics does not tell us when an equilibrium will be attained.
4. First law of thermodynamics does not give information about why there can not be 100 percent conversion of heat into work

SECOND LAW OF THERMODYNAMICS

Statement(I) : Second law of thermodynamics states that heat can never be converted into work with 100% efficiency

Statement(II) : No engine in this world can be constructed which operates in cycles and converts all the heat from source to work.

Statement(III) : No refrigeratator can be designed which operates in cycles and rejects heat from sink to source, perpetually (self - functioning).

Entropy : Entropy is the direct measurment of randomness or disorderness. Entropy is an extensive property & it is a state function

$ds = \frac{dq_{rev}}{T}$ for reversible process. entropy is related with complexity of the molecule within the system.

EtOH > MeOH

$C_2H_6(g) > C_2H_5(g)$

$N_2O_4 > NO_2$

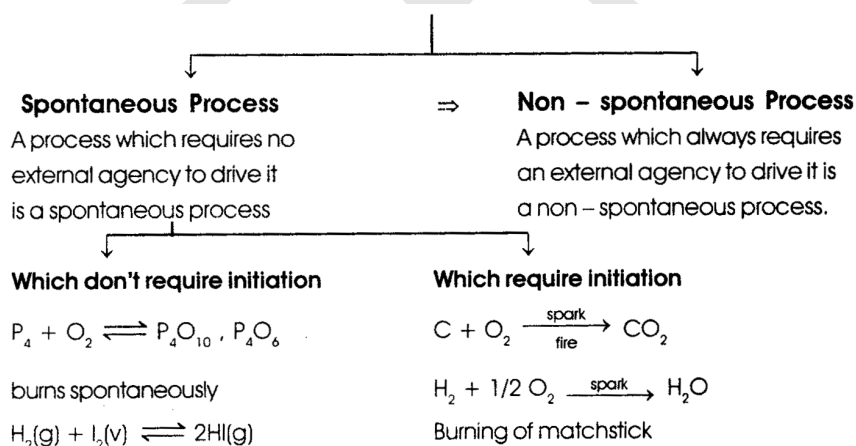
$O_2 > N_2$ (molecular wt.)

Gas > Liq > Amorphous solid > crystalline solid

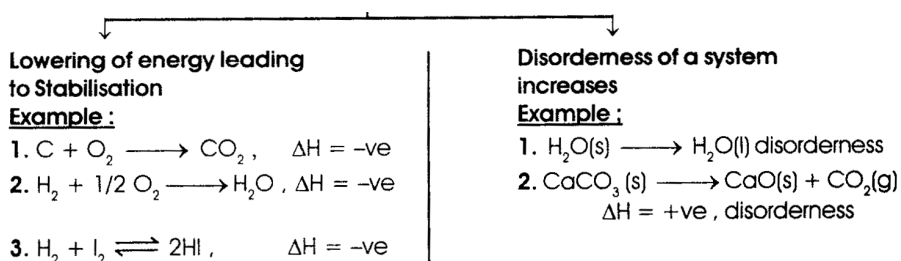
Entropy always increases in the following process

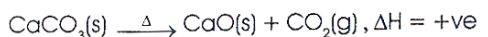
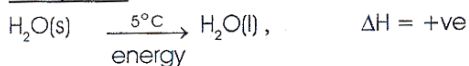
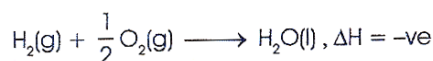
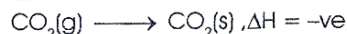
- (1) $s \rightarrow l, l \rightarrow g, s \rightarrow g,$
- (2) Isothermal expansion of ideal gas.
- (3) Mixing of two non reacting gases.
- (4) In chemical reaction in which
 $\Delta n_g > 0$
- (5) Heating of any substance

CLASSIFICATION OF PROCESS BASED ON SPONTANEITY



Why Spontaneity



Exception : \Rightarrow Exception

$$\Delta G = \Delta H - T\Delta S$$

Points to ponder :

Why a system always moves towards disorderness ?

Answer : A system moves towards disorderness because the probability of moving towards disorderness is very high.

DISORDERNESS**For Reversible process :**

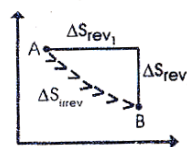
$$\Delta S = \frac{Q_{\text{reversible}}}{T} \quad Q_{\text{reversible}} = \text{constant}$$

$$\Delta S = \int \frac{dQ_{\text{reversible}}}{T} \quad Q_{\text{reversible}} = \text{Variable}$$

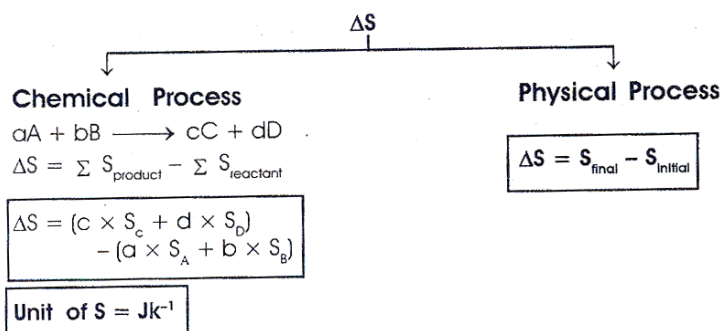
Note : Irreversible process

$$\Delta S_{\text{irreversible}} = \Delta S_{\text{rev1}} + \Delta S_{\text{rev2}}$$

$$\Delta S_{\text{irreversible}} = \frac{Q_{\text{rev1}}}{T_1} + \frac{Q_{\text{rev2}}}{T_2}$$



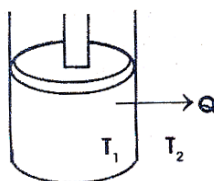
The entropy change for an irreversible process can be calculated by substituting it with equivalent reversible process. Both will have same entropy change.

**ENTROPY CHANGE OF UNIVERSE**

$$\Delta S_{\text{system}} = \frac{-Q}{T_1}$$

$$\Delta S_{\text{surrounding}} = \frac{+Q}{T_1}$$



$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$$



SPONTANEITY

1. $\Delta S_{\text{universe}} > 0 \Rightarrow$ **Spontaneous**
2. $\Delta S_{\text{universe}} = 0 \Rightarrow$ **Equilibrium**
3. $\Delta S_{\text{universe}} < 0 \Rightarrow$ **Non-spontaneous.**

ENTROPY CHANGE (ΔS)

In a reversible process	In an irreversible process
 $\Delta S_{\text{system}} = -Q/T$ $\Delta S_{\text{surrounding}} = +Q/T$ $\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$ $= -Q/T + Q/T$ <div style="border: 1px solid black; padding: 2px; display: inline-block;">$\Delta S_{\text{universe}} = 0$</div> <p>In a reversible process $\Delta S_{\text{universe}}$ is zero. Hence system is always in equilibrium.</p>	 $T_1 > T_2$ $1/T_1 < 1/T_2 \text{ or } 1/T_2 - 1/T_1 > 0.$ <p>Now, $\Delta S_{\text{system}} = -Q/T_1$</p> $\Delta S_{\text{surrounding}} = +Q/T_2$ $\Delta S_{\text{universe}} = Q/T_2 - Q/T_1$ $\Delta S_{\text{universe}} = Q(1/T_2 - 1/T_1)$ <div style="border: 1px solid black; padding: 2px; display: inline-block;">$\Delta S_{\text{universe}} > 0$</div> <p>In an irreversible process $\Delta S_{\text{universe}} > 0$ hence the process is always spontaneous</p>

CALCULATION OF ENTROPY CHANGE

(A) General heating or cooling

$$ds = \frac{dq_{\text{rev}}}{T}$$

$$\Delta S = \int ds = \int \frac{dq_{\text{rev}}}{T} = \int_{T_1}^{T_2} nC_V dT$$

If C is temperature independent

$$\Delta S = nC \ln \frac{T_2}{T_1}$$

If C is a function of Temperature

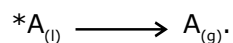
$$C = a + bT$$

$$\Delta S = n \int_{T_1}^{T_2} \left(\frac{a + bT}{T} \right) dT$$

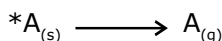
$$\Delta S = n \left[a \ln \frac{T_2}{T_1} + b(T_2 - T_1) \right]$$

(B) In phase transformation

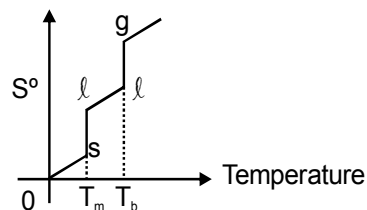
$$\Delta S_{\text{fus}} = \frac{q_{\text{rev}}}{T_m} = \frac{n \Delta H_{\text{fusion}}}{T_m}$$



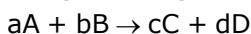
$$\Delta S_{\text{vap}} = \frac{n\Delta H_{\text{vap}}^{\circ}}{T_B}$$



$$\Delta S_{\text{sub}} = \frac{n\Delta H_{\text{sub}}^{\circ}}{T}$$



(C) Entropy change during chemical reaction.



$$\Delta S^{\circ} = \text{entropy of product} - \text{entropy of reactant}$$

For any chemical reaction

$$\int_{\Delta S_1}^{\Delta S_2} ds = \int_{T_1}^{T_2} \frac{C_d T}{T}$$

$$\Delta S_2 - \Delta S_1 = C_V \ln \frac{T_2}{T_1}$$

(D) Calculation of entropy change during expansion/compression of ideal gas from P_1, V_1, T_1 to P_2, V_2, T_2

From 1st law of thermodynamics

$$dE = dq + dW$$

$$dq = -dW + dE$$

$$TdS = PdV + nC_V dT$$

$$dS = \frac{P}{T} dV + nC_V \frac{dT}{T}$$

$$dS = \frac{nR}{V} dV + \frac{nC_V dT}{T}$$

$$\Delta S = \int dS = nR \ln \frac{V_2}{V_1} + nC_V \ln \frac{T_2}{T_1}$$

$$\Delta S = nR \ln \frac{V_2}{V_1} + nC_V \ln \frac{T_2}{T_1}$$

For ideal gas

$$\Delta S = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2} \cdot \frac{T_2}{T_1}$$

$$= nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2} + nR \ln \frac{T_2}{T_1}$$

$$= nR \ln \frac{P_1}{P_2} + (C_V + R)n \ln \frac{T_2}{T_1}$$

$$\Delta S = nR \ln \frac{P_1}{P_2} + nC_P \ln \frac{T_2}{T_1}$$

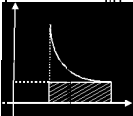
Conclusion ΔS increasesWhen $T \uparrow$ $V \uparrow$ & $P \downarrow$ If C_v is temperature dependent

$$\Delta S = n \int C_v \frac{dT}{T} + nR \ln \frac{V_2}{V_1}$$

$$\Delta S = n \int \frac{(a+bT)}{T} dT + nR \ln \frac{V_2}{V_1}$$

$$\Delta S = n \left[a \ln \frac{T_2}{T_1} + b(T_2 - T_1) \right] + nR \ln \frac{V_2}{V_1}$$

Calculation of entropy change during isothermal Expansion;

Process	ΔS_{system}	ΔS_{surr}	ΔS_{Total}
1. Reversible $\Delta E = q_{\text{rev}} + w_{\text{rev}}$ $\Delta E = 0$	$\Delta S_{\text{system}} = \frac{q_{\text{rev}}}{T} = -\frac{w_{\text{rev}}}{T} = nR \ln \frac{V_2}{V_1} = +ve$	$\Delta S_{\text{surr}} = -\frac{q_{\text{process}}}{T} = -nR \ln \frac{V_2}{V_1} = -ve$	0
2. Irreversible Free expansion $\Delta E = 0, w = 0$	$nR \ln \frac{V_2}{V_1}$	0	> 0
3. Irreversible expansion $\Delta E = q_{\text{irr}} + w_{\text{irr}}$ 	$nR \ln \frac{V_2}{V_1}$	$\Delta S = -\frac{q_{\text{irr}}}{T} = \frac{w_{\text{irr}}}{T} = -ve$	> 0


because $\frac{w_{\text{rev}}}{T} = \frac{-nRT}{T} \ln \frac{V_2}{V_1} = -nR \ln \frac{V_2}{V_1}$

$$nR \ln \frac{V_2}{V_1} = \frac{-w_{\text{rev}}}{T}$$

$$w_{\text{rev}} > w_{\text{irr}}$$

$$\Delta S_{\text{total}} = +ve$$

Calculation of entropy change during isothermal compression.

Process	ΔS_{syst}	ΔS_{surr}	ΔS_{Total}
1. Reversible Process	$\Delta S_{\text{syst}} = \frac{q_{\text{rev}}}{T} = -\frac{w_{\text{rev}}}{T} = nR \ln \frac{V_2}{V_1} = -ve$	$\Delta S_{\text{surr}} = -\frac{q_{\text{process}}}{T} = \frac{w_{\text{rev}}}{T} = -nR \ln \frac{V_2}{V_1} = +ve$	0
2. Irreversible compression B 	$\Delta S_{\text{sys}} = nR \ln \frac{V_2}{V_1} = -ve$	$\Delta S_{\text{surr}} = \frac{-q_{\text{irr}}}{T} = \frac{w_{\text{irr}}}{T} = +ve$	> 0

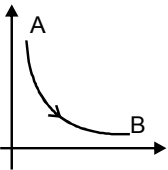
$$q_{\text{irr}} + w_{\text{irr}} = 0$$

$$|w_{\text{irr}}| > |w_{\text{rev}}|$$

$$< 0 \quad > 0$$

$$\Rightarrow |q_{\text{irr}}| > |q_{\text{rev}}|$$

Calculation of entropy change during for adiabatic expansion of ideal gas.

1. Process 	$\Delta S_{\text{sys}} = \frac{q_{\text{rev}}}{T}$ $= nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$ <p style="text-align: center;"> \downarrow -ve \downarrow +ve $= 0$ </p>	$\Delta S_{\text{surr}} = \frac{-q_{\text{process}}}{T} = 0$	0
2. Irreversible Process free expansion	$nR \ln \frac{V_2}{V_1}$	0	+ ve

For reversible process

$$\Delta E = q_{\text{rev}} + w_{\text{rev}}$$

$$\quad \quad \quad \parallel$$

$$\quad \quad \quad 0$$

$$nC_V dT = -100 \text{ (let)}$$

$$(T_2 - T_1) = K (-100)$$

Where K is constant

$$T_2 = T_1 - 100K$$

For irreversible process

$$\Delta E = q_{\text{irr}} + w_{\text{irr}}$$

$$\quad \quad \quad \parallel$$

$$\quad \quad \quad 0$$

$$T_2' - T_1 = -90K$$

$$T_2' = T_1 - 90K$$

This means that the final temperature of irreversible process is greater than reversible process.

$$\Delta S = nC_V \ln \frac{T_2'}{T_1} + nR \ln \frac{V_2}{V_1}$$

\downarrow -ve \downarrow +ve

$$= nC_V \ln \frac{T_2'}{T_1} - nC_V \ln \frac{T_2}{T_1}$$

$$= nC_V \ln \frac{T_2'}{T_2}$$

$$\Rightarrow T_2' > T_2$$

$$\Rightarrow \Delta S = +ve$$

$$\Delta S_{\text{surr}} = \frac{-q_{\text{process}}}{T} = 0$$

$$\Rightarrow \Delta S_{\text{total}} = +ve$$

Calculation of entropy change in adiabatic compression.

1. Reversible	$\Delta S = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$ <p style="text-align: center;"> \downarrow +ve \downarrow -ve $= 0$ </p>	0	0
2. Irreversible adiabatic compression	<p>For reversible process</p> $\Delta E = q_{\text{rev}} + w_{\text{rev}}$ $\Delta E = 100$ $dT = 100\text{K}$ <p>For irreversible process</p> $i_{\text{irr}} \quad \Delta E = q_{\text{irr}} + w_{\text{irr}}$ $= 110$	0	0

dT = 110

For reversible

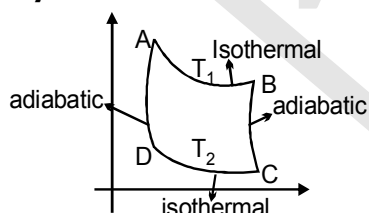
$$(T_2 - T_1) = 100\text{K}$$

$$T_2 = T_1 + 100\text{K}$$

for irreversible $T'_2 = T_1 + 110\text{K}$

$$T'_2 > T_2$$

$$\begin{aligned} \Delta S_{\text{irr}} &= nC_V \ln \frac{T'_2}{T_1} + nR \ln \frac{V_2}{V_1} \\ &= nC_V \ln \frac{T'_2}{T_1} - nC_V \ln \frac{T_2}{T_1} \\ &= nC_V \ln \frac{T'_2}{T_2} > 0 \end{aligned}$$

CARNOT CYCLE**Carnot cycle is based on 4 reversible process.****(1) Reversible isothermal expansion from A to B.**

$$\Delta E_{AB} = 0,$$

$$W_{AB} = -nRT_1 \ln \frac{V_2}{V_1}$$

(2) Reversible adiabatic expansion from B to C

$$\Delta E_{BC} = nC_V(T_2 - T_1)$$

$$W_{BC} = \Delta E_{BC}$$

(3) Isothermal compression from C to D

$$\Delta E_{CD} = 0,$$

$$W_{CD} = -nRT_2 \ln \frac{V_4}{V_3}$$

$$q_{CD} = -W_{CD}$$

(4) Adiabatic compression from D to A.

$$\Delta E_{DA} = nC_V(T_1 - T_2)$$

$$W_{DA} = \Delta E_{DA}$$

$$\Delta E_{\text{Cycle}} = 0$$

$$W_{\text{cycle}} = -nRT_1 \ln \frac{V_2}{V_1} + nC_V(T_2 - T_1) - nRT_2 \ln \frac{V_4}{V_3} + nC_V(T_1 - T_2)$$

$$= -nR \left[T_1 \ln \frac{V_2}{V_1} + T_2 \ln \frac{V_4}{V_3} \right]$$

$$\text{For BC, } T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1}$$

$$\text{For DA, } T_1 V_1^{\gamma-1} = T_2 V_4^{\gamma-1}$$

$$\left(\frac{V_2}{V_1} \right)^{\gamma-1} = \left(\frac{V_3}{V_4} \right)^{\gamma-1} \Rightarrow \boxed{\frac{V_2}{V_1} = \frac{V_3}{V_4}}$$

$$W_{\text{cycle}} = -nR(T_1 - T_2) \ln V_2/V_1$$

Efficiency of any engine may be given as

$$\eta = \frac{|w_{\text{net}}|}{q_1 \text{ (Heat given)}}$$

$$\eta = \frac{nR(T_1 - T_2) \ln \frac{V_2}{V_1}}{nRT_1 \ln \frac{V_2}{V_1}} = \frac{(T_1 - T_2)}{T_1}$$

$$\boxed{\eta = 1 - \frac{T_2}{T_1}}$$

$$\Delta E_{\text{cycle}} = q_{\text{cyc}} + w_{\text{cycle}}$$

$$w_{\text{cycle}} = -q_{\text{cycle}} = \frac{(q_1 + q_2)}{q_1}$$

$$\frac{q_1 + q_2}{q_1} = 1 - \frac{T_2}{T_1}$$

$$1 + \frac{q_2}{q_1} = 1 - \frac{T_2}{T_1}$$

$$\Rightarrow \frac{q_2}{T_2} + \frac{q_1}{T_1} = \sum \frac{q_{\text{rev}}}{T} = 0$$

$$\Rightarrow \oint ds = 0$$

This means ΔS is a state function

Gibb's Free Energy (G)

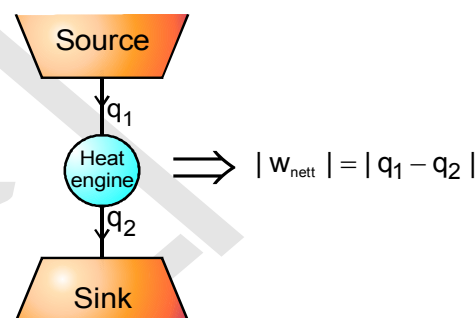
$$G_{\text{system}} = H_{\text{system}} - TS_{\text{system}}$$

$$W = W_{\text{expansion}} + W_{\text{non-expansion}}$$

$$W_{\text{non-expansion}} = w_{\text{useful}} \text{ (useful work)}$$

$$\Delta G = W_{\text{non expansion}} = W_{\text{useful}}$$

All those energy which is available with the system which is utilized in doing useful work is called Gibb's free energy :



• R_x :

1. $\Delta G_{\text{system}} = \Delta H_{\text{system}} - T\Delta S_{\text{system}} = -T\Delta S_{\text{universe}} = W_{\text{non expansion}} = W_{\text{useful}}$

2. $\Delta G_{\text{system}} = -T\Delta S_{\text{universe}}$

3. (a) $\Delta S_{\text{universe}} > 0$ or $\Delta G_{\text{system}} < 0 \Rightarrow$ Spontaneous

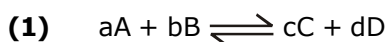
(b) $\Delta S_{\text{universe}} = 0$ or $\Delta G_{\text{system}} = 0 \Rightarrow$ Equilibrium

(c) $\Delta S_{\text{universe}} < 0$ or $\Delta G_{\text{system}} > 0 \Rightarrow$ Non-Spontaneous

ΔH	ΔS	ΔG	Result (T) .
+ve	+ve	-ve	T should be high for spontaneity
+ve	-ve	+ve	Non-spontaneous at all temperature
-ve	+ve	-ve	Spontaneous at all temperature
-ve	-ve	-ve	T should be low for spontaneity

APPLICATION OF (ΔG)

• R_x :



ΔG° = Standard Gibbs free energy change (P = 1 atm, 298 K)

ΔG = Gibbs free energy change at any condition.

NERST EQUATION

$\Delta G = \Delta G^\circ + 2.303 RT \log Q$; Q = Reaction Quotient

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

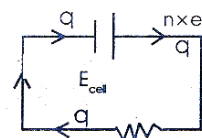
At equilibrium, $\Delta G = 0$ and $Q = K_{\text{eq}}$.

$$0 = \Delta G^\circ + 2.303 RT \log k_{\text{eq}}$$

$$\Delta G^\circ = -2.303 RT \log k_{\text{eq}}$$

$$\sum G^\circ(\text{product}) - \sum G^\circ(\text{Reactant}) = -2.303 RT \log k_{\text{eq}}$$

$$\Delta H^\circ - T\Delta S^\circ = -2.303 RT \log k_{\text{eq}}$$



(2) $W_{\text{cell}} = q \times E$

$$\Delta G = -W_{\text{cell}}$$

$$\Delta G = -q \times E_{\text{cell}}$$

Now, one mole e^- have charge 96500 coulomb = 1 Faraday (F)

n mole of e^- will have charge = $n \times F$ or $q = n \times F$

$$\Delta G = -nFE_{\text{cell}}$$

$$\Delta G^\circ = -nFE_{\text{cell}}^\circ$$

THIRD LAW OF THERMODYNAMICS

$$\lim_{T \rightarrow 0} S = 0$$

Third law of thermodynamics states that as the temperature approaches absolute zero, the entropy of perfectly crystalline substance also approaches zero.

APPLICATION OF THIRD LAW OF THERMODYNAMICS

$$\Delta S = \int_{T_1}^{T_2} \frac{dQ_{\text{reversible}}}{T}$$

$$S_{T_2} - S_{T_1} = \int_{T_1}^{T_2} \frac{dQ_{\text{reversible}}}{T}$$

Taking $T_2 = T$ and $T_1 = 0^\circ\text{K}$.

$$S_T - 0 = \int_{T_0}^T \frac{dQ_{\text{reversible}}}{T} \Rightarrow S_T = \int_{T_0}^T \frac{dQ_{\text{reversible}}}{T} \quad \text{For perfectly crystalline substance}$$

- The entropy of perfectly crystalline substance can be determined using third law of thermodynamics.
- or
- With the help of third law of thermodynamics we can calculate the exact value of entropy.

 ΔG AND NON PV WORK (NON EXPANSION/COMPRESSION)

$(\Delta G)_{T,P}$ is a measure of useful work a non PV work (non expansion work) that can be produced by a chemical transformation.e.g.electrical work .

For reversible reaction at constant T & P

$$dU = dq + dW_{\text{total}}$$

$$dU = dq + dW_{P,V} + dW_{\text{non } P,V}$$

$$dU = T.dS - P. dV + dW_{\text{non } P,V}$$

$$dU + P.dV = T. dS + dW_{\text{non } P,V}$$

$$dH = T.dS + dW_{\text{non } P,V}$$

$$(dG_{\text{sys}})_{T,P} = dW_{\text{non } P,V}$$

$$(\Delta G_{\text{sys}})_{T,P} = W_{\text{non } P,V}$$

Useful work done on the system = increase in Gibb's energy of system at constant T & P.

$$-(\Delta G_{\text{sys}})_{T,P} = -W_{\text{non } P,V}$$

$$-(\Delta G_{\text{sys}})_{T,P} = -W_{\text{by, non } P,V}$$

Useful work done by the system = decrease in Gibb's energy of system at constant T & P .

If $(\Delta G_{\text{sys}})_{T,P} = 0$, then system is unable to deliver useful work.

THERMODYNAMIC RELATION

For reversible process in which non expansion work is not possible

$$dU = dq + dW$$

$$dU = T.dS - P.dV$$

$$H = U + PV$$

$$dH = dU + P.dV + V.dP$$

$$dH = T.dS - PdV + PdV + V.dP$$

$$dH = T.dS + V.dP$$

$$G = H - TS$$

$$dG = dH - T.dS - S.dT$$

$$dG = T.dS + V.dP - T.dS - S.dT$$

$$dG = V.dP - S.dT \quad \text{For a particular system (s/ℓ/g)}$$

- (1) At constant temperature $dG = V.dP$ or $\left(\frac{\partial G}{\partial P}\right)_T = V$

(A) For a system is s/ℓ phase

$$\int dG = \int V.dP$$

$$\Delta G = V\Delta P$$

(B) For an ideal gas, expansion/compression :-

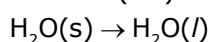
$$\int dG = \int V.dP = \int \frac{nRT}{P} dP$$

$$\Delta G = nRT \ln \frac{P_2}{P_1} = nRT \ln \frac{V_1}{V_2}$$

- (2) At constant pressure : $dG = -S.dT$ or $\left(\frac{\partial G}{\partial T}\right)_P = -S$

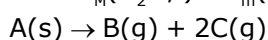
* For phase transformation/chemical reaction

$$d(\Delta G) = \Delta V.dP - \Delta S dT$$

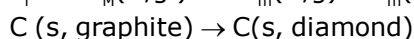


$$\Delta V = V_m(H_2O, l) - V_m(H_2O, s)$$

$$\Delta S = S_m(H_2O, l) - S_m(H_2O, s)$$



$$\Delta_r S = S_m(B, g) + 2S_m(C, g) - S_m(A, s)$$



$$\Delta V = V_m(C, \text{diamond}) - V_m(C\text{-graphite})$$

At constant temperature:-

$$d(\Delta G) = \Delta V. dP$$

$$\Delta G_{P_2} - \Delta G_{P_1} = \Delta V[P_2 - P_1]$$

At constant pressure

$$\int d(\Delta_r G) = -\int (\Delta_r S) dT$$

$$\Delta_r G_{T_2} - \Delta_r G_{T_1} = -\Delta_r S(T_2 - T_1)$$

Solved Problems

Ex.1 Show that pressure of a fixed amount of an ideal gas is a state function $V = \frac{nRT}{p}$

Sol. $\left(\frac{\partial V}{\partial T}\right)_p = \frac{nR}{p} \Rightarrow \frac{\partial}{\partial p} \left[\left(\frac{\partial V}{\partial T}\right)_p \right]_T = \frac{-nR}{p^2}$

$$\left(\frac{\partial V}{\partial T}\right)_T = -\frac{nRT}{p^2} \quad \frac{\partial}{\partial T} \left[\left(\frac{\partial V}{\partial p}\right)_T \right]_p = \frac{-nR}{p^2}$$

Ex.2 Calculate work done for the expansion of a substance 3m^3 to 5m^3 against.

- (a) Constant pressure = 10^5 Pa
 (b) A variable pressure = $(10 + 5V)$ Pa

Sol. (a) $W = -PdV = -10^5(5-3) = -2 \times 10^5 \text{ J}$

(B) $W = -\int (10 + 5V)dV$

$$= -\left(10V + \frac{5V^2}{2}\right)_3^5 = -\left[(10 \times 2) + \frac{5}{2} \times 16\right]$$

$$= -(20 + 40) = -60$$

Ex.3 Calculate change in internal energy for a gas under going from state-I (300 K , $2 \times 10^{-2} \text{ m}^3$) to state -II (400 K , $4 \times 10^{-2} \text{ m}^3$) for one mol. of vanderwaal gas.

- (a) If gas is ideal [$C_v = 12 \text{ J/K/mol}$]
 (b) If gas is real

{ Given : $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$

$C_v = 12 \text{ J/k/mol}$

$a = 2 \text{ J.m.}/\text{mol}^2$ } (Not in JEE)

Sol. (a) $\Delta U = nC_v(T_2 - T_1) = 1 \times 12 \times 100 = 1200 \text{ J}$

(b) $du = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$

$$\left[\begin{array}{l} \left(P + \frac{a}{V^2}\right)(V-b) = RT \\ P = \frac{RT}{V-b} - \frac{a}{V^2} \\ \Rightarrow \frac{\partial P}{\partial T} = \frac{R}{V-b} \end{array} \right]$$

$$= \left(\frac{\partial U}{\partial T}\right)_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]dV$$

$$= C_V dT + \frac{a}{V^2} dV$$

$$dU = C_V(T_2 - T_1) + a \left(\frac{1}{V_1} - \frac{1}{V_2} \right)$$

$$= C_V(100) + a \left(\frac{1}{4} \right) \times 10^2$$

$$= 12 \times 100 + 2 \left(\frac{1}{4} \right) \times 100 = 1250$$

Ex.4 One mole of an ideal gas is expanded isothermally at 300 K from 10 atm to 1 atm. Calculate q , w , ΔU & ΔH under the following conditions.

(i) Expansion is carried out reversibly.

(ii) Expansion is carried out irreversibly

Sol. Isothermal process

(i) For ideal gas $\Delta U = 0$ $\Delta H = 0$

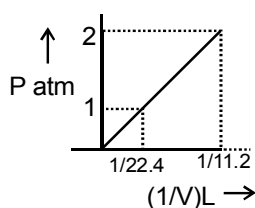
$q = -w$

$$w_{\text{rev}} = -nRT \ln \frac{P_1}{P_2} = -1 \times R \times 300 \ln \frac{10}{1} = -690.9R$$

$$(ii) W_{\text{irrev}} = -P_{\text{ext}}(V_2 - V_1) = -P_{\text{ext}} \left(\frac{nRT}{P_2} - \frac{nRT}{P_1} \right)$$

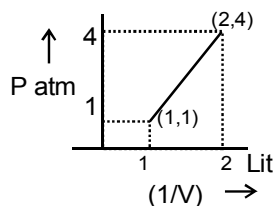
$$= -1 \times 1 \times R \times 300 \left[\frac{1}{1} - \frac{1}{10} \right] = -270R$$

Ex. 5 Calculate work done for an ideal gas ($\ln 2 = 0.7$)



$$w = -nRT \ln \frac{P_1}{P_2} = -22.4 \times \ln \frac{1}{2} = 22.4 \times 0.7 = 15.68$$

Ex. 6 Calculate $w = ?$ ($\ln 2 = 0.7$)



Sol. P - V Relation from plot

$$y = mx + C$$

$$1 = m + C \quad \dots\dots\dots(1)$$

$$4 = 2m + C \quad \dots\dots\dots(2)$$

$$\Rightarrow m = 3, C = -2$$

$$\text{Hence, } P = \frac{3}{V} - 2$$

$$\begin{aligned} w_{\text{rev}} &= -\int P dv = -\int_1^{1/2} \left(\frac{3}{V} - 2 \right) dv = -\int_1^{1/2} (3 \ln v - 2v) \\ &= -\left[3 \ln \frac{1}{2} - 2 \left(\frac{1}{2} - 1 \right) \right] = 3 \times 0.7 - 1 = 1.1 \text{ lit atm} \end{aligned}$$

Ex. 7 One mole an ideal gas is expanded from (10 atm, 10 lit) to (2 atm, 50 litre) isothermally. First against 5 atm then against 2 atm. Calculate work done in each step and compare it with single step work done with 2 atm.

Sol.

$$(i) \quad P_1 V_1 = P_2 V_2$$

$$\text{Vol. of system at 5 atm} = \frac{10 \times 10}{5} = 20 \text{ lit.}$$

$$w_{\text{irrev}} = -P_{\text{ext}}(V_2 - V_1) = -5(20 - 10) = -50 \text{ atm lit.}$$

(ii) Work done against 2 atm

$$\begin{array}{ccc} P_1 & V_1 & \longrightarrow P_2 \quad V_2 \\ 5 \text{ atm} & 20 \text{ lit} & 2 \text{ atm} \quad 50 \text{ lit} \end{array}$$

$$w_{\text{irrev}} = -P_{\text{ext}}(V_2 - V_1) = -2(50 - 20) = -60 \text{ atm lit.}$$

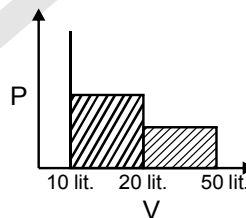
$$w_{\text{total}} = -50 - 60 = -110 \text{ atm lit.}$$

Total work done in single step.

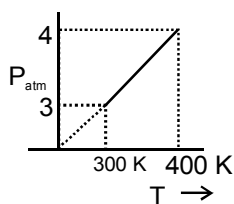
$$\begin{array}{ccc} P_1 & V_1 & \longrightarrow P_2 \quad V_2 \\ 10 \text{ atm} & 10 \text{ lit} & 2 \text{ atm} \quad 50 \text{ lit} \end{array}$$

$$w = -2(50 - 10) = -80 \text{ lit}$$

magnitude of work done in more than one step is more than single step work done.



Ex 8. For 1 mole of monoatomic gas. Calculate w , ΔU , ΔH , q



Sol. Isochoric process

$$w = 0$$

$$q = dU = C_v (T_2 - T_1) = \frac{3}{2} \times (400 - 300) = 150 R$$

$$\Delta H = C_p \Delta T = \frac{5}{2} R (400 - 300) = 250 R$$

Ex 9 One mole of an non linear triatomic ideal gas is expanded adiabatically at 300 K from 16 atm to 1 atm.

Calculate Work done under the following conditions.

(i) Expansion is carried out reversibly.

(ii) Expansion is carried out irreversibly

Sol. $q = 0$

$$w = \Delta U = C_v (T_2 - T_1)$$

$$C_v \text{ for triatomic non linear gas} = 3R$$

(i) For rev. process.

$$P_1^{1-\gamma} T_1^\gamma = P_2^{1-\gamma} T_2^\gamma \quad r = \frac{4}{3} \quad T_2 = T_1 \left(\frac{P_1}{P_2} \right)^{\frac{1-\gamma}{\gamma}} = 300(16)^{\frac{1-\frac{4}{3}}{\frac{4}{3}}} = 300(16)^{\frac{1-\frac{4}{3}}{\frac{4}{3}}} = 300(2^4)^{-1/4} = 150K$$

$$\Delta U = w = 3R (150 - 300) = -450 R$$

(ii) $n = 1$

$$-P_{\text{ext}} (V_2 - V_1) = C_v (T_2 - T_1)$$

$$-P_{\text{ext}} \left(\frac{RT_2}{P_2} - \frac{RT_1}{P_1} \right) = 3R(T_2 - T_1)$$

$$-1 \left(\frac{RT_2}{1} - \frac{RT_1}{16} \right) = 3R(T_2 - T_1)$$

$$-\frac{R}{16} (16T_2 - T_1) = 3R(T_2 - T_1)$$

$$-16T_2 + T_1 = 48 T_2 - 48 T_1$$

$$49 T_1 = 64 T_2$$

$$T_2 = \frac{49}{64} \times 300$$

$$T_2 = 229.69$$

$$w_{\text{irr}} = C_v(T_2 - T_1) + 3R (229.69 - 300) = -210.93 R$$

Ex 10 One mole of an non linear triatomic ideal gas is compressed adiabatically at 300 K from 1 atm to 16 atm.

Calculate Work done under the following conditions.

(i) Expansion is carried out reversibly.

(ii) Expansion is carried out irreversibly.

Sol. $q = 0$ Adiabatic process

(i) $w_{\text{rev}} = \Delta U = C_v(T_2 - T_1)$

$$P^{1-\gamma} T^\gamma = K$$

$$T_2 = 300 \left(\frac{1}{16} \right)^{\frac{1-4/3}{4/3}} = 600 K$$

$$w = 3R (600 - 300) = 900 R$$

(ii) $w_{\text{irr}} = -P_{\text{ext}}(V_2 - V_1) = -P_{\text{ext}} \left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right)$

$$-P_{\text{ext}} \left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right) = C_v(T_2 - T_1)$$

$$-16 \left(\frac{RT_2}{16} - \frac{RT_1}{1} \right) = 3R(T_2 - T_1)$$

$$-(T_2 - 16 T_1) = 3R (T_2 - T_1)$$

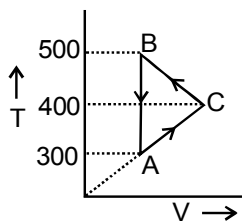
$$-T_2 + 16 T_1 = 3T_2 - 3T_1$$

$$4T_2 = 19 T_1$$

$$T_2 = \frac{19}{4} \times 300 = 1425 K$$

$$w = \Delta U = 3R (1425 - 300) = 3375 R$$

Ex 11. Calculate work done is process BC for 1 mol of an ideal gas if total 600 cal heat is released by the gas in whole process



Sol. For cyclic process

$$dU = 0$$

$$q = -w$$

$$PV_1 = 1 \times R \times 300$$

$$PV_2 = 1 \times R \times 400$$

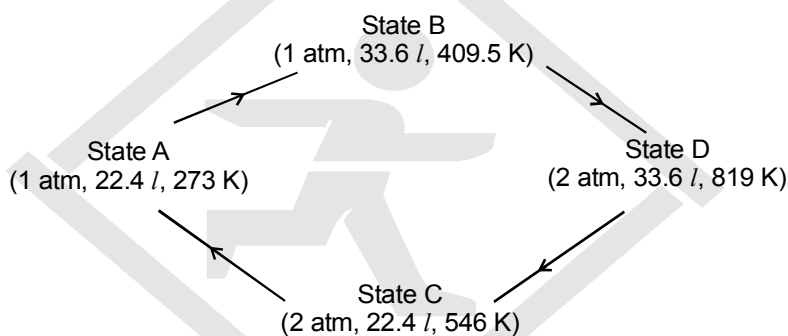
$$\Rightarrow P(V_2 - V_1) = R(400 - 300)$$

$$q = -(w_{BA} + w_{AC} + w_{CB})$$

$$-600 = -(0 + (-) 2 \times (400 - 300) + w_{CB})$$

$$w_{CB} = 800 \text{ cal}$$

Ex 12 Calculate entropy change in each step for an ideal gas (monoatomic)



Sol. $\Delta S_{A-B} = nC_p \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2} = nC_p \ln \frac{409.5}{273} = C_p \ln \frac{3}{2}$

$$\Delta S_{AC} = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} = C_v \ln \frac{546}{273} = C_v \ln 2$$

$$\Delta S_{C-D} = nC_p \ln \frac{T_2}{T_1} + nR \ln \frac{P_1}{P_2} = nC_p \ln \frac{819}{546} = C_p \ln \frac{3}{2}$$

$$\Delta S_{AC} = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

$$= nC_v \ln \frac{819}{409.5} = C_v \ln \frac{3}{2}$$

Ex 13 One mole of an ideal gas is expanded isothermally at 300 K from 10 atm to 1 atm. Find the values of

ΔS_{sys} , ΔS_{surr} & ΔS_{total} under the following conditions.

(i) Expansion is carried out reversibly.

(ii) Expansion is carried out irreversibly

(iii) Expansion is free.

Sol. (i) $\Delta S_{\text{sys}} = nC_p/n \frac{T_2}{T_1} + nR/n \frac{P_1}{P_2} = 0 + R/n10 = R \ln 10$

$$\Delta S_{\text{surr.}} = -\Delta S_{\text{sys}} = -R/n10$$

$$\Delta S_{\text{total}} = 0$$

(ii) $\Delta S_{\text{sys}} = R \ln 10$

$$\Delta S_{\text{surr.}} = \frac{-q_{\text{irr}}}{T}$$

$$\Delta U = 0 = q + w$$

$$q_{\text{irr}} = p_{\text{ext}}(v_2 - v_1)$$

$$q_{\text{irr}} = p_{\text{ext}} \left[\frac{RT}{p_2} - \frac{RT}{p_1} \right] = RT \left[\frac{1}{1} - \frac{1}{10} \right]$$

$$= RT \times \frac{9}{10} = \frac{9}{10} \times R \times 300 = 270R$$

$$\Delta S_{\text{surr}} = \frac{-q_{\text{irr}}}{T} = \frac{-9R}{10}$$

$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = R \ln 10 - \frac{9R}{10}$$

(iii) Free expansion $\Delta T = 0$

$$w = 0$$

$$q = 0$$

$$\Delta S_{\text{sys}} = R \ln 10$$

$$\Delta S_{\text{surr}} = \frac{-q_{\text{irr}}}{T} = 0$$

$$\Delta S_{\text{total}} = R \ln 10$$

Ex 14 One mole of a non linear triatomic ideal gas is expanded adiabatically at 300 K from 16 atm to 1 atm. Find the values of ΔS_{sys} , ΔS_{surr} & ΔS_{total} under the following conditions.

(i) Expansion is carried out reversibly.

(ii) Expansion is carried out irreversibly

(iii) Expansion is free.

Sol. For non-linear tri-atomic ideal gas

$$C_v = 3R, C_p = 4R$$

$$(i) \quad \Delta S_{\text{sys}} = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} = 0$$

$$q = 0$$

$$\Delta S_{\text{surr}} = -\Delta S_{\text{sys}} = 0$$

$$\Delta S_{\text{total}} = 0$$

(ii) First of all we will have to calculate the temperature of the gas after it has undergone the said adiabatic

reversible expansion we have $q = 0$

$$\Delta U = q + w$$

$$nC_v (T_2 - T_1) = -p_{\text{ext}} (V_2 - V_1)$$

$$3R(T_2 - 300) = -1 \left[\frac{RT_2}{p_2} - \frac{RT_1}{2} \right] = -R \left[\frac{T_2}{1} - \frac{300}{16} \right]$$

$$T_2 = 229.68 \text{ K}$$

$$\Delta S_{\text{sys}} = nC_p \ln \frac{T_2}{T_1} + nR \ln \frac{p_1}{p_2}$$

$$= 4R \ln \frac{229.68}{300} + R \ln \frac{16}{1} = -1.068 R + 2.77 R = 1.702 R$$

$$\Delta S_{\text{surr}} = \frac{-q_{\text{irr}}}{T} = 0$$

$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} = 1.702 R$$

(iii) In free adiabatic expansion we have

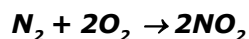
$$w = 0$$

$$q = 0 \quad \Delta T = 0$$

$$\Delta S_{\text{sys}} = nR \ln \frac{p_1}{p_2} = R \ln 16 = 2.77R$$

$$\Delta S_{\text{surr}} = \frac{-q_{\text{irr}}}{T} = 0$$

$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} = 2.77R$$

Ex 15 For the reaction

Given : at 1 atm, 300 K

$$S_{\text{N}_2} = 180 \text{ J/mol/K}$$

$$C_p(\text{N}_2) = 30 \text{ J/mol/K}$$

$$S_{\text{O}_2} = 220 \text{ J/mol/K}$$

$$C_p(\text{O}_2) = 30 \text{ J/mol/K}$$

$$S_{\text{NO}_2} = 240 \text{ J/mol/K}$$

$$C_p(\text{NO}_2) = 40 \text{ J/mol/K}$$

Calculate

$$(i) \quad \Delta S_{300 \text{ K}, 1 \text{ atm}}$$

$$(ii) \quad \Delta S_{400 \text{ K}, 1 \text{ atm}}$$

$$(iii) \quad \Delta S_{300 \text{ K}, 5 \text{ atm}}$$

$$(iv) \quad \Delta S_{400 \text{ K}, 5 \text{ atm}}$$

Sol. (i) $(\Delta S_r)_{300} = 2S_{\text{NO}_2} - 2S_{\text{O}_2} - S_{\text{N}_2} = 2 \times 240 - 2 \times 220 - 180 = -140 \text{ J mol}^{-1}\text{K}^{-1}$
 $(\Delta C_p)_r = 2C_p(\text{NO}_2) - 2C_p(\text{O}_2) - C_p(\text{N}_2) = 2 \times 40 - 2 \times 30 - 30 = -10 \text{ J mol}^{-1}\text{K}^{-1}$

$$(ii) \quad (\Delta S_r)_{400} = (\Delta S_r)_{300} + (\Delta C_p)_r \ln \frac{T_2}{T_1} = -140 - 10 \ln \frac{4}{3} = -142.88 \text{ J mol}^{-1}\text{K}^{-1}$$

$$(iii) \quad (\Delta S_r)_{300 \text{ K}, 5 \text{ atm}} = (\Delta S_r)_{300 \text{ K}, 1 \text{ atm}} + \Delta n_g R \ln \frac{p_1}{p_2} = -140 + (-1)R \ln \frac{1}{5} = -140 + R \ln 5$$

$$= -140 + 8.314 \ln 5 = -126.62 \text{ J mol}^{-1}\text{K}^{-1}$$

$$(iv) \quad (\Delta S_r)_{400 \text{ K}, 5 \text{ atm}} = (\Delta S_r)_{400 \text{ K}, 1 \text{ atm}} - R \ln \frac{1}{5} = -142.88 + R \ln 5 = -129.5 \text{ J mol}^{-1}\text{K}^{-1}$$

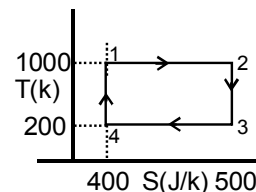
Ex 16 From the T-S diagram of a reversible carnot engine calculate :

(i) **efficiency**

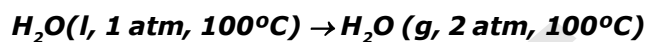
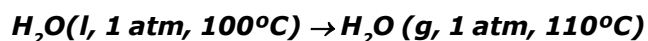
(ii) **workdone per cycle**

(iii) **Heat taken from the source and rejected to sink**

(iv) **In order to illuminate 10000 bulbs of 40 watt power each calculate the no. of cycle per second the above must go through.**

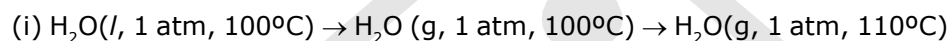


- Sol.** (i) $\eta = \frac{1000 - 200}{1000} = 80\%$
- (ii) $q_{\text{rev1-2}} = \int T ds = 1000 \times 100 \text{ J}$
 $q_{3-4} = \int T ds = -200 \times 100 \text{ J}$
 $q_{\text{net}} = 800 \times 100 = 80 \text{ kJ}$
 $W = -80 \text{ kJ}$
- (iii) $10^5 \text{ J},$
 $2 \times 10^4 \text{ J}$
- (iv) 5

Ex 17 Calculate entropy change

$$\Delta H_{\text{vap}} = 40 \text{ kJ/mol} \quad C_p(l) = 75 \text{ J/mol/K} \quad C_p(g) = 35 \text{ J/mol/K}$$

Sol. For 1 mol



(A) (B) (C)

$$\Delta S_{A \rightarrow B} = \frac{\Delta H_{\text{vap}}}{T} = \frac{40 \times 1000}{373}$$

$$\Delta S_{S \rightarrow C} = nC_p(g) \ln \frac{T_2}{T_1} = 1 \times 35 \ln \frac{383}{373}$$



(A) (B) (C)

$$\Delta S_{A \rightarrow B} = \frac{\Delta H_{\text{vap}}}{T} = \frac{40.000}{373}$$

$$\Delta S_{S \rightarrow C} = nR \ln \frac{P_2}{P_1} = 1 \times R \ln \frac{1}{2}$$

CLASS ROOM ASSIGNMENT

1. A certain electric motor produced 15 kJ of energy each second as mechanical work and lost 2 kJ as heat to the surroundings. What is the change in the internal energy of the motor and its power supply each second ?

[Ans. -17 kJ]

Sol.

2. The internal energy change in the conversion of 1.0 mole of the calcite form of CaCO_3 to the aragonite form is +0.21 kJ. Calculate the enthalpy change when the pressure is 1.0 bar ; given that the densities of the solid are 2.71 g cm^{-3} and 2.93 g cm^{-3} respectively. [Ans. $0.20972 \text{ kJ mol}^{-1}$]

Sol.

3. Work done in expansion of an ideal gas from 4 litre to 6 litre against a constant external pressure of 2.5 atm was used to heat up 1 mole of water at 293 K. If specific heat of water is $4.184 \text{ J g}^{-1} \text{ K}^{-1}$ what is the final temperature of water ?

[Ans. 299.723 K]

Sol.

4. 10 g of argon gas is compressed isothermally and reversibly at a temperature of 27°C from 10 L to 5 L. Calculate q , W , ΔU and ΔH for this process. $R = 2.0 \text{ cal K}^{-1} \text{ mol}^{-1}$, $\log_{10} 2 = 0.30$, Atomic wt. of Ar = 40.

[Ans. $q = -$

103.991 cal , $\Delta H = 0$, $\Delta U = 0$, $w = 103.991 \text{ cal}$]

Sol.

5.

Water is boiled under a pressure of 1.0 atm. When an electric current of 0.50 A from a 12 V supply is passed for 300 s through a resistance in thermal contact with it, it is found that 0.789 g of water is vaporized. Calculate the molar internal energy and enthalpy changes at boiling point (373.15 K.)

[Ans. 37.5 kJ/mol , 40.6 kJ/mol]

Sol.

6.

An aeroplane weighing 63,000 kg flies up from sea level to a height of 8000 metre. Its engine run with pure normal octane (C_8H_{18}) has a 30% of efficiency. Calculate the fuel cost of the flight, if octane sells at Rs 3/- per litre. Given density of octane = 0.705 g mL^{-1} , heat of combustion of octane = $1300 \text{ kcal mol}^{-1}$ ($g = 981 \text{ cm/sec}^2$)

[Ans. Rs. 1472.4]

Sol.

7.

What is the temperature at which average K.E. of an ideal gas molecule is 1 eV.

[Ans. 11594 K]

Sol.

8.

For a reaction at 25°C enthalpy change (ΔH) and entropy change (ΔS) are $-11.7 \times 10^3 \text{ J mol}^{-1}$ and $-105 \text{ J mol}^{-1} \text{ K}^{-1}$ respectively. Find out whether this reaction is spontaneous or not?

[Ans. not spontaneous]

Sol.

9.

Calculate the entropy change when 1 kg of water is heated from 27°C to 200°C forming super heated steam under constant pressure. Given specific heat of water = 4180 J/kg-K and specific heat of steam = $1670 + 0.49 T \text{ J/kg-K}$ and latent heat of vaporization = $23 \times 10^5 \text{ J/kg}$

[Ans. 7522.50 J]

Sol.

10.

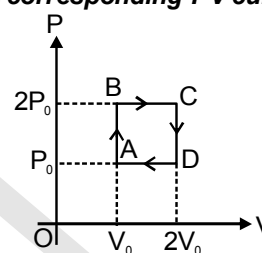
Derive a relation showing reversible work of expansion from volume V_1 to V_2 by 'n' moles of a real gas obeying van der Waals' equation at temperature T where volume occupied by molecules may be taken as negligible in comparison to total volume of gas.

$$[\text{Ans. } W = -nRT \log \frac{V_2}{V_1} - n^2 a \left[\frac{1}{V_2} - \frac{1}{V_1} \right] J]$$

Sol.

11.

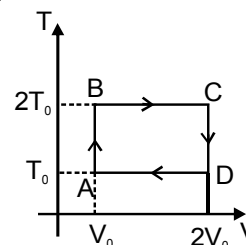
Find out the work done in the given graph. Also draw the corresponding T-V curve and P-T curve.



Sol.

12.

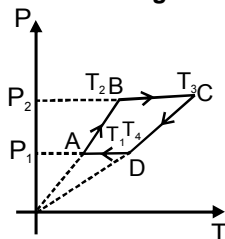
T-V curve of cyclic process is shown below, number of moles of the gas n find the total work done during the cycle.



Sol.

13.

P-T curve of a cyclic process is shown. Find out the work done by the gas in the given process if number of moles of the gas are n .



Sol.

16.

From the equation $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$. Prove

that for ideal gas $\left(\frac{\partial U}{\partial V}\right)_T = 0$.

Sol.

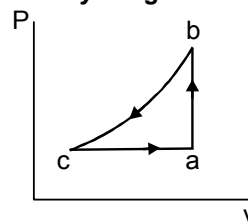
14.

Consider the cyclic process ABCA on a sample of 2.0 mol of an ideal gas as shown in figure. The temperatures of the gas at A and B are 300 K and 500 K respectively. A total of 1200 J heat is withdrawn from the sample in the process. Find the work done by the gas in part BC. Take $R = 8.3$ J/mol-K.

Sol.

17.

A sample of an ideal gas is taken through the cyclic process abca (figure). It absorbs 50 J of heat during the part ab, no heat during bc and reflects 70 J of heat during ca. 40 J of work is done on the gas during the part bc. (a) Find the internal energy of the gas at b and c if it is 1500 J at a. (b) Calculate the work done by the gas during the part ca.



Sol.

15.

1 gm water at 100°C is heated to convert into steam at 100°C at 1 atm. Find out change in internal energy of water. It is given that volume of 1 gm water at 100°C = 1 cc. volume of 1 gm steam at 100°C = 1671 cc. Latent heat of vaporization = 540 cal/g. (Mechanical equivalent of heat $J = 4.2$ J/cal.)

Sol.

18.

The internal energy of a monatomic ideal gas is $1.5 nRT$. One mole of helium is kept in a cylinder of cross-section 8.5 cm^2 . The cylinder is closed by a light frictionless piston. The gas is heated slowly in a process during which a total of 42 J heat is given to the gas. If the temperature rises through 2°C , find the distance moved by the piston. Atmospheric pressure = 100 kPa .

Sol.

19.

A sample of an ideal gas has pressure p_0 , volume v_0 and temperature T_0 . It is isothermally expanded to twice its original volume. It is then compressed at constant pressure to have the original volume V_0 . Finally, the gas is heated at constant volume to get the original temperature. (a) Show the process in a $V - T$ diagram (b) Calculate the heat absorbed in the process.

Sol.

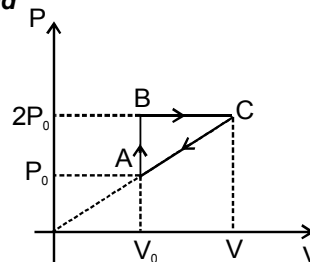
20.

A sample of ideal gas ($f = 5$) is heated at constant pressure. If an amount 140 J of heat is supplied to the gas, find (a) the change in internal energy of the gas (b) the work done by the gas.

Sol.

21.

n moles of a diatomic gas has undergone a cyclic process ABC as shown in figure. Temperature at A is T_0 . Find



(i) Volume at C ?

(ii) Maximum temperature ?

(iii) Total heat given to gas ?

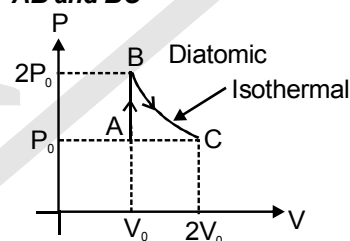
(iv) Is heat rejected by the gas, if yes how much heat is rejected ?

(v) Find out the efficiency

Sol.

22.

P - V curve of a diatomic gas is shown in the figure. Find the total heat given to the gas in the process AB and BC



Sol.

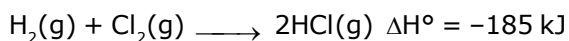
EXERCISE – I**OBJECTIVE PROBLEMS (JEE MAIN)**

1. Out of boiling point (I), entropy (II), pH (III) and density (IV), Intensive properties are :

- (A) I, II (B) I, II, III
(C) I, III, IV (D) All of these

Sol.

2. Consider the reaction at 300 K

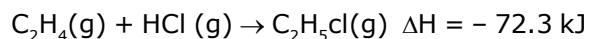


If 3 mole of H_2 completely react with 3 mole of Cl_2 to form HCl. What is ΔU° for this reaction ?

- (A) 0 (B) -185 kJ
(C) 555 kJ (D) None of these

Sol.

3. Ethyl chloride ($\text{C}_2\text{H}_5\text{Cl}$), is prepared by reaction of ethylene with hydrogen chloride :

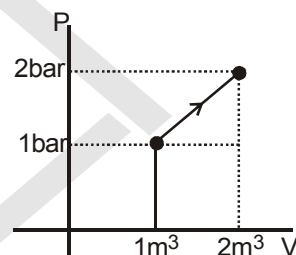


What is the value of ΔE (in kJ), if 70 g of ethylene and 73 g of HCl are allowed to react at 300 K.

- (A) -69.8 (B) -180.75
(C) -174.5 (D) -139.6

Sol.

4. What is ΔU for the process described by figure. Heat supplied during the process $q = 100 \text{ kJ}$.



- (A) +50 kJ (B) -50 kJ
(C) -150 kJ (D) +150 kJ

Sol.

5. One mole of ideal gas is allowed to expand reversibly and adiabatically from a temperature of 27°C . If the work done by the gas in the process is 3 kJ, the final temperature will be equal to ($C_v = 20 \text{ J/K mol}$)

- (A) 100 K (B) 450 K
(C) 150 K (D) 400 K

Sol.

7. The heat capacity of liquid water is 75.6 J/mol K , while the enthalpy of fusion of ice is 6.0 kJ/mol . What is the smallest number of ice cubes at 0°C , each containing 9.0 g of water, needed to cool 500 g of liquid water from 20°C to 0°C ?

- (A) 1 (B) 7
(C) 14 (D) None of these

Sol.

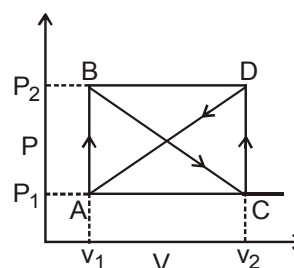
6. What is the change in internal energy when a gas contracts from 377 ml to 177 ml under a constant pressure of 1520 torr, while at the same time being cooled by removing 124 J heat?

[Take : (1 L atm) = 100 J]

- (A) -24 J (B) -84 J (C) -164 J (D) -248 J

Sol.

8. An ideal gas is taken around the cycle ABCDA as shown in figure. The net work done during the cycle is equal to :



- (A) zero (B) positive
(C) negative (D) we cannot predict

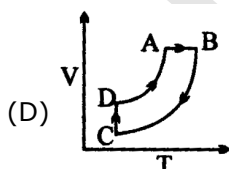
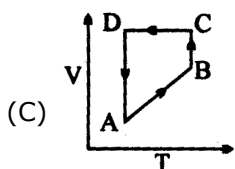
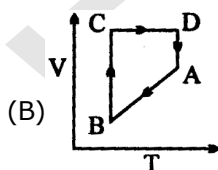
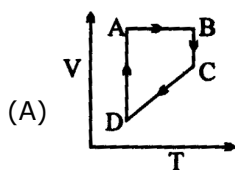
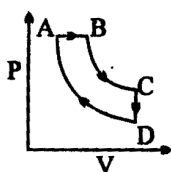
Sol.

9. Molar heat capacity of water in equilibrium with ice at constant pressure is

- (A) zero (B) ∞
 (C) $40.45 \text{ kJ K}^{-1} \text{ mol}^{-1}$ (D) $75.48 \text{ JK}^{-1} \text{ mol}^{-1}$

Sol.

10. A cyclic process ABCD is shown in PV diagram for an ideal gas. Which of the following diagram represents the same process ?

**Sol.**

11. A diatomic ideal gas initially at 273 K is given 100 cal heat due to which system did 209 J work. Molar heat capacity (C_m) of gas for the process is :

- (A) $\frac{3}{2}R$ (B) $\frac{5}{2}R$
 (C) $\frac{5}{4}R$ (D) $5R$

Sol.

12. One mole of an ideal monoatomic gas expanded irreversibly in two stage expansion.

- State-1 (8.0 bar, 4.0 litre, 300 K)
 State-2 (2.0 bar, 16 litre, 300 K)
 State-3 (1.0 bar, 32 litre, 300 K)

Total heat absorbed by the gas in the process is :

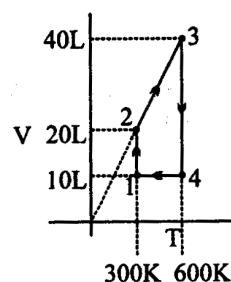
- (A) 116 J (B) 40 J
 (C) 4000 J (D) None of these

Sol.

13. For an ideal monoatomic gas during any process $T = kV$, find out the molar heat capacity of the gas during the process. (Assume vibrational degree of freedom to be active)

- (A) $\frac{5}{2}R$ (B) $3R$ (C) $\frac{7}{2}R$ (D) $4R$

Sol.



$\ln 2 = 0.7$

- (A) -600 cal (B) -660 cal
(C) +660 cal (D) +600 cal

Sol.

14. A gas ($C_{v,m} = \frac{5}{2}R$) behaving ideally was allowed to expand reversibly and adiabatically from 1 litre to 32 litre. Its initial temperature was 327°C . The molar enthalpy change (in J/mole) for the process is

- (A) -1125 R (B) -575 R
(C) -1575 R (D) None of these

Sol.

15. What is the net work done (**in calories**) on 1 mole of monoatomic ideal gas in a process described by 1,2,3,4 in given V-T graph.

Use : $R = 2\text{ cal/mole K}$

16. Two moles of an ideal gas ($C_v = \frac{5}{2}R$) was compressed adiabatically against constant pressure of 2 atm. Which was initially at 350 K and 1 atm pressure. The work involve in the process is equal to

- (A) 250 R (B) 300 R (C) 400 R (D) 500 R

Sol.

17. An insulated container of gas has two chambers separated by an insulating partition. One of the chambers has volume V_1 and contains ideal gas at pressure P_1 and temperature T_1 . The other chamber has volume V_2 and contains ideal gas at pressure P_2 and temperature T_2 . If the partition is removed without doing any work on the gas, the final equilibrium temperature of the gas in the container will be

- (A) $\frac{T_1 T_2 (P_1 V_1 + P_2 V_2)}{P_1 V_1 T_2 + P_2 V_2 T_1}$ (B) $\frac{P_1 V_1 T_1 + P_2 V_2 T_2}{P_1 V_1 + P_2 V_2}$
 (C) $\frac{P_1 V_1 T_2 + P_2 V_2 T_1}{P_1 V_1 + P_2 V_2}$ (D) $\frac{T_1 T_2 (P_1 V_1 + P_2 V_2)}{P_1 V_1 T_1 + P_2 V_2 T_2}$

Sol.

18. The maximum efficiency of a heat engine operating between 100°C and 25°C is

- (A) 20.11% (B) 22.2%
 (C) 25.17% (D) None

Sol.

19. A heat engine operating between 227°C and 27°C absorbs 2 Kcal of heat from the 227°C reservoir reversibly per cycle. The amount of work done in one cycle is :

- (A) 0.4 Kcal (B) 0.8 Kcal (C) 4 Kcal (D) 8 Kcal

Sol.

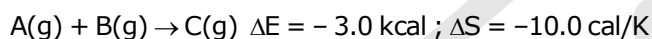
20. A reversible heat engine A (based on Carnot cycle) absorbs heat from a reservoir at 1000 K and rejects heat to a reservoir at T_2 . A second reversible engine B absorbs the same amount of heat as rejected by the engine A, from the reservoir at T_2 and rejects energy to a reservoir at 360 K . If the efficiencies of engines A

and B are the same then the temperature T_2 is

- (A) 680 K (B) 640 K (C) 600 K (D) None

Sol.

21. For the reaction at 300 K



value of ΔG is

- (A) -600 cal (B) -6600 cal (C) -6000 cal (D) None

Sol.

22. The entropy change when two moles of ideal monoatomic gas is heated from 200 to 300°C reversibly and isochorically

(A) $\frac{3}{2}R \ln \left(\frac{300}{200} \right)$ (B) $\frac{5}{2}R \ln \left(\frac{573}{273} \right)$

(C) $3R \ln \left(\frac{573}{473} \right)$ (D) $\frac{3}{2}R \ln \left(\frac{573}{473} \right)$

Sol.

23. What is the free energy change (ΔG) when 1.0 mole of water at 100°C and 1 pressure is converted into steam at 100°C and 1 atm pressure ?

- (A) 80 cal (B) 540 cal (C) 620 cal (D) zero

Sol.

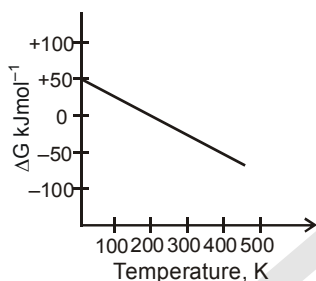
24. What if the free energy change (ΔG) when 1.0 mole of water at 100°C and 1 atm pressure is converted into steam at 100°C and 2 atm pressure ?

- (A) zero cal (B) 540 cal
(C) 517.13 cal (D) 510 cal

Sol.



25. What can be concluded about the values of ΔH and ΔS from this graph ?



- (A) $\Delta H > 0$, $\Delta S > 0$ (B) $\Delta H > 0$, $\Delta S < 0$
 (C) $\Delta H < 0$, $\Delta S > 0$ (D) $\Delta H < 0$, $\Delta S < 0$

Sol.

26. If $\Delta H_{\text{vapourisation}}$ of substance X (l) (molar mass : 30 g/mol) is 300 J/g at its boiling point 300 K, then molar entropy change for reversible condensation process is

- (A) 30 J/mol.K (B) -300 J/mol K
 (C) -30 J/mol K (D) None of these

Sol.

27. Pressure of 10 moles of an ideal gas is changed from 2 atm to 1 atm against constant external pressure without change in temperature. If surrounding temperature (300K) and pressure (1 atm) always remains constant then calculate total entropy change ($\Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$) for given process.

[Given : $\ln 2 = 0.70$ and $R = 8.0 \text{ J/mol/K}$]

- (A) 56 J/K (B) 14 J/K
 (C) 16 J/K (D) None of these

Sol.

28. The enthalpy of tetramerization of X in gas phase ($4X(g) \rightarrow X_4(g)$) is -100 kJ/mol at 300 K. The enthalpy of vaporisation for liquid X and X_4 are respectively 30 kJ/mol and 72 kJ/mol respectively. ΔS for tetramerization of X in liquid phase is -125 J/K mole at 300 K. What is the ΔG at 300 K for tetramerization of x in liquid phase.

- (A) -52 kJ/mol (B) -89.5 kJ/mol
 (C) -14.5 kJ/mol (D) None of these

Sol.

Sol.

29. The change in entropy of 2 moles of an ideal gas upon isothermal expansion at 243.6 K from 20 litre until the pressure becomes 1 atm, is :

- (A) 1.385 cal/K (B) -1.2 cal/k
(C) 1.2 cal/K (D) 2.77 cal/K

Sol.

30. Standard entropy of X_2 , Y_2 and XY_3 are 60, 40 and 50 $\text{JK}^{-1} \text{mol}^{-1}$, respectively. For the reaction,

$\frac{1}{2}X_2 + \frac{3}{2}Y_2 \rightarrow XY_3$, $\Delta H = -30 \text{ kJ}$ to be at equilibrium, the temperature will be

- (A) 1250 K (B) 500 K (C) 750 K (D) 1000 K

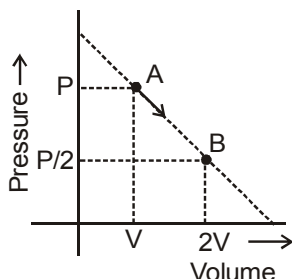
31. When two equal sized pieces of the same metal at different temperatures T_h (hot piece) and T_c (cold piece) are brought into contact into thermal contact and isolate from it's surrounding. The total change in entropy of system is given by

- (A) $C \ln \frac{T_c + T_h}{2T_c}$ (B) $C \ln \frac{T_2}{T_1}$
(C) $C \ln \frac{(T_c + T_h)^2}{2T_h \cdot T_c}$ (D) $C \ln \frac{(T_c + T_h)^2}{4T_h \cdot T_c}$

Sol.

EXERCISE – II**OBJECTIVE PROBLEMS (JEE ADVANCED)**

1. An ideal gas is taken from state A (Pressure P , Volume V) to the state B (Pressure $P/2$, Volume $2V$) along a straight line path in PV diagram as shown in the adjacent figure.



Select the correct statement (s) among the following

- (A) The work done by gas in the process A to B exceeds the work that would be done by it if the system were taken from A to B along the isotherm.
- (B) In the T-V diagram, the path AB become part of parabola.
- (C) In the P-V diagram, the path AB becomes a part of hyperbola.
- (D) In going from A to B, the temperature T of the gas first increases to a maximum value then decreases.

Sol.

2. The normal boiling point of a liquid 'A' is 350 K. ΔH_{vap} at normal boiling point is 35 kJ/mole. Pick out the correct statement (s). (Assume ΔH_{vap} to be independent of pressure).

- (A) $\Delta S_{\text{vaporisation}} > 100 \text{ J/K mole}$ at 350 K and 0.5 atm
- (B) $\Delta S_{\text{vaporisation}} < 100 \text{ J/K mole}$ at 350 K and 0.5 atm
- (C) $\Delta S_{\text{vaporisation}} < 100 \text{ J/K mole}$ at 350 K and 2 atm
- (D) $\Delta S_{\text{vaporisation}} = 100 \text{ J/K mole}$ at 350 K and 2 atm

Sol.

3. Which of the following statement(s) is/are false :

- (A) $\Delta_r S$ for $\frac{1}{2}\text{N}_2(\text{g}) \rightarrow \text{N}(\text{g})$ is positive
- (B) ΔG_{system} is always zero for a reversible process in a closed system
- (C) ΔG° for an ideal gas is a function of temperature and pressure
- (D) entropy of a closed system is always maximized at equilibrium

Sol.

4. Which statement is/are correct :

- (A) Final temperature in reversible adiabatic expansion is lesser than in irreversible adiabatic expansion.
- (B) When heat is supplied to an ideal gas in an isothermal process, kinetic energy of gas will increase
- (C) When an ideal gas is subjected to adiabatic expansion it gets cooled
- (D) Entropy increases in atomisation of dihydrogen

Sol.

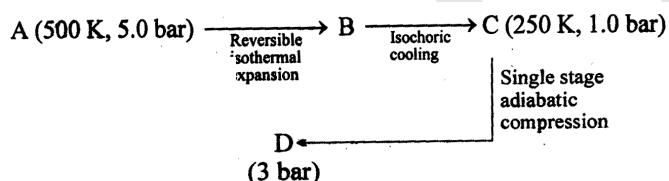
5. Which is /are correct statement.

(A) $W_{\text{adiabatic}} > W_{\text{isothermal}}$ in an ideal gas compression from same initial state to same final volume(B) The volume of $\gamma \left(\gamma = \frac{C_p}{C_v} \right)$ remains constant for diatomic gas at all temperature

(C) Entropy increases when an ideal gas expanded isothermally.

(D) $\Delta_r H$ & $\Delta_r S$ both are +ve for the decomposition of $\text{MgCO}_3(\text{s})$.

Sol.

6. Two moles of an ideal gas ($C_{v,m} = 3/2 R$) is subjected to following change of state.

The correct statement is/are :

(A) The pressure at B is 2.0 bar

(B) The temperature at D is 450 K

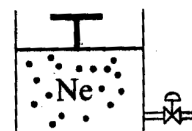
(C) $\Delta H_{CD} = 1000 R$ (D) $\Delta U_{BC} = 375 R$

Sol.

7. In isothermal ideal gas compression

(A) w is +ve(B) ΔH is zero(C) ΔS_{gas} is +ve(D) ΔG is +ve

Sol.

8. A piston cylinder device initially contains 0.2 m^3 neon (assume ideal) at 200 kPa inside at $T_1^\circ\text{C}$. A valve is now opened and neon is allowed to escape until the volume reduces to half the initial volume.At the same time heat transfer with outside at $T_2^\circ\text{C}$ ensures a constant temperature inside.

Select correct statement(s) for given process

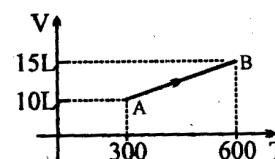
(A) ΔU must be zero(B) ΔU may not be zero(C) q may be +ve(D) q may be -ve

Sol.

9. If one mole monoatomic ideal gas was taken through process AB as shown in figure, the select correct option (s).

(A) $w_{AB} = -1496.52 \text{ J}$ (B) $q_{AB} = 5237.82 \text{ J}$ (C) $\Delta H_{AB} = 3741.3 \text{ J}$ (D) ΔS_{AB} is +ve

Sol.



- 10.** Which of the following statement(s) is/are correct
 (A) Reversible isothermal compression of an ideal gas represents the limiting minimum value of the workdone ($|w|$) by the surrounding on the system.
 (B) In an irreversible process, the cyclic integral of work is not zero.
 (C) For thermodynamic changes in adiabatic process

$$T^{\left(\frac{C_{p,m}}{R}\right)}. P = \text{constant}$$

- (D) Work done by 1 mole of a real (vander waals) gas

$$W = -RT \ln \frac{V_2 - b}{V_1 - b} - a \left[\frac{V_1 \times V_2}{V_2 - V_1} \right]$$

Sol.

ASSERTION REASON :

- (A) Statement-I is true, statement-II is true and statement-II is correct explanation for statement-I
 (B) Statement-I is true, statement-II is true and statement-II is NOT the correct explanation for statement-I
 (C) Statement-I is false, statement-II is true.
 (D) Statement-I is true, statement-II is false.

11. Statement-1 : There is no change in enthalpy of an ideal gas during compression at constant temperature.

Statement-II : Enthalpy of an ideal gas is a function of temperature and pressure.

Sol.

12. Statement-1 : Due to adiabatic free expansion, temperature of a real gas always increases

Statement-II : If a real gas is at inversion temperature then no change in temperature is observed in adiabatic free expansion.

Sol.

13. Statement-1 : There is no change in enthalpy of an ideal gas during compression at constant pressure.

Statement-II : Enthalpy of an ideal gas is a function of temperature .

Sol.

14. Statement-1 : Two reversible adiabats can never intersect.

Statement-II : Efficiency of carnot engine cannot be one.

Sol.

15. Statement-1 : Adiabatic process must be isentropic process.

Statement-II : $dS = \frac{dq_{rev}}{T}$

Sol.

16. Statement-1 : During irreversible adiabatic expansion of ideal gas entropy must increase.

Statement-II : Increase in entropy of the system due to expansion is only partially compensated by decrease in temperature.

Sol.

17. What will be the final pressure in container B.

(A) 2 atm (B) 8 atm (C) 16 atm (D) 32 atm

Sol.

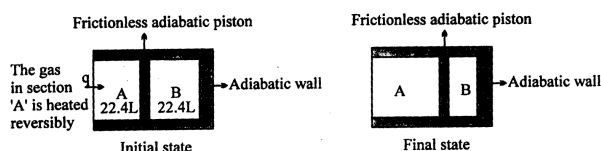
18. Final temperature in container A will be

(A) 1638 K (B) 6988 K (C) 3274 K (D) 51 K

Sol.

COMPREHENSION-I

A cylindrical container of volume 44.8 litres is containing equal no. of moles (in integer no.) of an ideal monoatomic gas in two sections A and B separated by an adiabatic frictionless piston as shown in figure. The initial temperature and pressure of gas in both section is 27.3 K and 1 atm. Now gas in section 'A' is slowly heated till the volume of section B becomes $(1/8)^{\text{th}}$ of initial volume.



Given : $R = 2 \text{ cal/mol-K}$, $C_{v,m}$ of monoatomic gas $= \frac{3}{2}R$,
At 1 atm & 0°C ideal gas occupy 22.4 litre.

19. Change in enthalpy for section A in Kcal.

(A) 48.3 (B) 80.53 (C) 4.83 (D) 8.05

Sol.

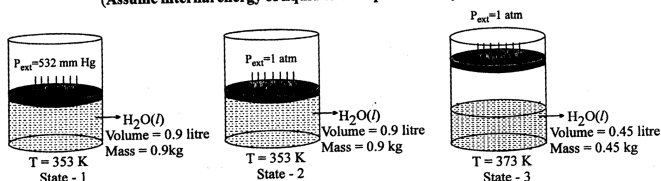
COMPREHENSION - 2

The vapour pressure of $\text{H}_2\text{O}(l)$ at 353 K is 532 mm Hg. The external pressure on $\text{H}_2\text{O}(l)$ taken in a cylinder fitted with frictionless movable piston initially containing 0.9 L (= 0.9 kg) of $\text{H}_2\text{O}(l)$ at 353 K is increased to 1 atm. Temperature remained constant. Now, heat is supplied keeping pressure constant till 0.45 L of $\text{H}_2\text{O}(l)$ (= 0.45 kg) is evaporated to form $\text{H}_2\text{O}(g)$ at 373 K. Carefully observe the diagrams provided and from given data, answer the following questions.

Given: Specific heat of $\text{H}_2\text{O} = 4.2 \text{ J/gm } ^\circ\text{C}$
 ΔH_{vap} at 373 K and 1 atm = +40 kJ/mol
 1 atm = 760 mm Hg

Use
 1 L atm = 100 Joule
 $R = 8 \text{ Joule/mole K}$

(Assume internal energy of liquid to be dependent only on temperature).



20. ΔH when system is taken from state 1 to state 2 (Joule) ?

- (A) zero (B) 0.27 (C) 27 (D) 90

Sol.

21. Total change in ΔU going from state 1 to 3 (kJ) ?

- (A) 75.6 (B) 1075.6 (C) 1001 (D) 74.6

Sol.

22. Total change in enthalpy going from state 1 to state 3 (kJ) ?

- (A) 75.6 (B) 1075.6 (C) 1001 (D) 74.6

Sol.

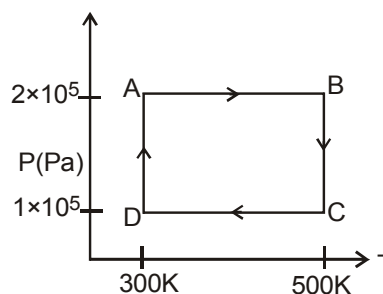
23. What is the work done in going state 1 to state 3 to in Joules.

- (A) zero (B) 45 (C) 90 (D) None

Sol.

COMPREHENSION-3

Two moles of helium gas are taken over the cycle ABCDA, as shown in the P-T diagram.



24. Assuming the gas to be ideal the work done by the gas in taking it from A to B is -

- (A) 200 R (B) 300 R (C) 400 R (D) 500 R

Sol.

25. The work done involved in taking it from D to A is

- (A) -414 R (B) +414 R (C) -690 R (D) +690 R

Sol.

26. The net work done involved in the cycle ABCDA is

- (A) zero (B) 276 R (C) 1076 R (D) 1904 R

Sol.

Match the column :

27. Match Column-I with Column-II

Column - I

(Ideal Gas)

(A) Reversible isothermal process

(B) Reversible adiabatic process

(C) Irreversible adiabatic process

(D) Irreversible isothermal process

Column-II

(Related equation)

(P) $W = 2.303 nRT \log (P_2/P_1)$

(Q) $W = nC_{v,m} (T_2 - T_1)$

(R) $PV = nRT$

(S) $W = - \int_{V_i}^{V_f} P_{\text{ext.}} dV$

Sol.

28. Match the column - I with column-II

Note that column - I may have more than one matching options in column-II

Column-I

(A) Reversible adiabatic compression

(B) Reversible vaporisation (Q) $\Delta S_{\text{system}} < 0$

(C) Free expansion of ideal gas in vacuum (R) $\Delta S_{\text{surrounding}} < 0$

(D) Dissociation of $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ (S) $\Delta S_{\text{surrounding}} = 0$

Sol.

29. Column I

(A) For the process

 $A(l) \rightarrow A(s)$, ΔH & ΔV may be(B) $A_2(s) + B_2(g) \rightleftharpoons C_2(s) + D_2(s)$ ΔH & ΔG may be

(C) For the given reaction

 $A_2(g) \rightleftharpoons B_2(g) + C_2(g)$, $E_{a(\text{forward})} = 50 \text{ kJ/mol}$ at very high temperature ΔH & ΔG are

(D) For the given reaction

 $A(g) \rightleftharpoons B(g)$, at very low temperature ΔH & ΔG may be**Sol.****Column-II**

(P) -ve, +ve

(Q) +ve, -ve

(R) +ve, +ve

(S) -ve, -ve

31. Column-I**(Related to process)**

(A) Fusion at melting point

(B) Vapourisation at boiling point

(C) Condensation at triple point

(D) Melting at normal boiling point

Column-II**(Related to system)**(P) $\Delta G = 0$ (Q) $\Delta G < 0$ (R) $\Delta S > 0$ (S) $\Delta H \approx \Delta U$ **Sol.****30.** Column - I may have more than one matching options in column-II**Column-I**

(A) Reversible condensation of vapour

(B) Irreversible adiabatic compression of an ideal gas

(C) Isothermal free expansion of an ideal gas in vacuum

(D) Reversible adiabatic expansion of an ideal gas

Sol.**Column-II**(P) $\Delta S_{\text{system}} > 0$ (Q) $\Delta S_{\text{system}} < 0$ (R) $\Delta S_{\text{surrounding}} < 0$ (S) $\Delta S_{\text{surrounding}} = 0$

EXERCISE – III**SUBJECTIVE PROBLEMS (JEE ADVANCED)****First law : Heat (q), work (w) and ΔU , ΔH**

1. In which of the following changes at constant pressure is work done by system on surrounding? By the surrounding on system?

Initial state	Final state
(i) $\text{H}_2\text{O}(\text{g})$	$\rightarrow \text{H}_2\text{O}(\text{l})$
(ii) $\text{H}_2\text{O}(\text{s})$	$\rightarrow \text{H}_2\text{O}(\text{g})$
(iii) $\text{H}_2\text{O}(\text{l})$	$\rightarrow \text{H}_2\text{O}(\text{s})$
(iv) $3\text{H}_2(\text{g}) + \text{N}_2(\text{g})$	$\rightarrow 2\text{NH}_3(\text{g})$
(v) $\text{CaCO}_3(\text{s})$	$\rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$

Sol.

2. The gas is cooled and loses 65 J of heat. The gas contracts as it cools and work done on the system equal to 20 J is exchanged with the surroundings. What are q, w and ΔE ?

Sol.

3. The enthalpy change for the reaction of 50 ml of ethylene with 50.0 ml of H_2 at 1.5 atm pressure is $\Delta H = -0.31$ KJ. What is the ΔE .

Sol.

4. The enthalpy of combustion of glucose is -2808 KJ mol^{-1} at 25°C . How many grams of glucose do you need to consume [Assume wt = 62.5 Kg]

(a) to climb a flight of stairs rising through 3M

(b) to climb a mountain of altitude 3000 M?

Assume that 25% of enthalpy can converted to useful work.

Sol.

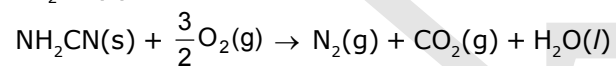
5. What is ΔE when 2.0 mole of liquid water vaporises at 100° ? The heat of vaporisation, ΔH_{vap} of water at 100°C is 40.66 KJ mol^{-1} .

Sol.

6. If 1.0 kcal of heat is added to 1.2 L of O_2 in a cylinder of constant pressure of 1 atm, the volume increases to 1.5 L. Calculate ΔE and ΔH of the process.

Sol.

7. When the following reaction was carried out in a bomb calorimeter, ΔE is found to be -742.7 kJ/mol of $NH_2CN(s)$ at 298 K.



Calculate ΔH_{298} for the reaction.

Sol.

8. When 1 mole of ice melt at 0°C and at constant pressure of 1 atm. 1440 calories of heat are absorbed by the system. The molar volumes of ice and water are 0.0196 and 0.0180 litre respectively. Calculate ΔH and ΔE for the reaction.

Sol.

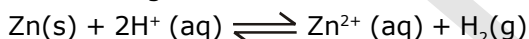
9. Water expands when it freezes. Determine amount of work in joules, done when a system consisting of 1.0 L of liquid water freezes under a constant pressure of 1.0 atm and forms 1.1 L of ice.

Sol.

10. Lime is made commercially by decomposition of limestone CaCO_3 . What is the change in internal energy when 1.00 mole of solid CaCO_3 ($V = 34.2 \text{ ml}$) absorbs 177.9 kJ of heat and decomposes at 25°C against a pressure of 1.0 atm to give solid CaO . (Volume = 16.9 ml) and CO_2 (g) ($V = 24.4 \text{ L}$)

Sol.

11. One mole of solid Zn is placed in excess of dilute H_2SO_4 at 27°C in a cylinder fitted with a piston. Find the value of ΔE , q and w for the process if the area of piston is 500 cm^2 and it moves out by 50 cm against a pressure of 1 atm during the reaction. The heat given to surrounding is 36.5 kJ.

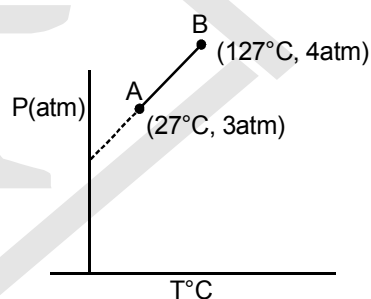


Sol.

12. Two mole of ideal diatomic gas ($C_{v,m} = 5/2 R$) at 300 K and 5 atm expanded irreversibly & adiabatically to a final pressure of 2 atm against a constant pressure of 1 atm. Calculate q , w , ΔH & ΔU .

Sol.

13. 4 moles of an ideal gas ($C_{v,m} = 15 \text{ J K}^{-1} \text{ mol}^{-1}$) is subjected to the following process represented on P – T graph from the data given. Find out
(a) The process is isochoric or not



(b) Calculate q , w , ΔU & ΔH for the process.

Sol.

14. Calculate the max. work done by system in an irreversible (single step) adiabatic expansion of 1 mole of a polyatomic gas ($\gamma = 1.33$) from 300 K and pressure 10 atm to 1 atm.

Sol.

15. 1 mole of CO_2 gas at 300 K is expanded under reversible adiabatic condition such that its volume becomes 27 times.

(a) What is the final temperature

(b) What is work done

Given $\gamma = 1.33$ and $C_v = 25.08 \text{ J mol}^{-1} \text{ K}^{-1}$ for CO_2

Sol.

16. Three moles of a ideal gas at 200K and 2.0 atm pressure undergo reversible adiabatic compression until the temperature becomes 250 K for the gas C_v is $27.5 \text{ JK}^{-1} \text{ mol}^{-1}$ in this temperature range. Calculate q , w , ΔU , ΔH and final V and final P .

Sol.

17. A sample of a fluorocarbon was allowed to expand to expand reversibly and adiabatically to twice its volume. In the expansion the temperature dropped from 298.15 K to 248.44 K. Assume the gas behaves perfectly Estimate the value of $C_{v,m}$.

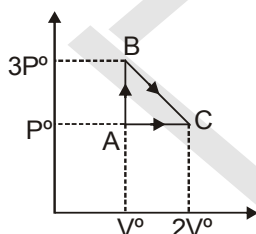
Sol.

18. Find the work done when one mole of the gas is expanded reversibly and isothermally from 5 atm to 1 atm at 25°C

Sol.

19. One mole of ideal monoatomic gas is carried through the reversible cyclic process as shown in figure. Calculate .

- work done by the gas.
- The heat changed by the gas in path CA and AB.
- Net heat absorbed by the gas in the path BC.



- The max. temperature attained by the gas during the cycle.

Sol.

20. One mole of an ideal monoatomic gas is carried through the reversible cycle of the given figure consisting of step A, B and C and involving state 1, 2 and 3.

Fill in the blank space in the table given below assuming

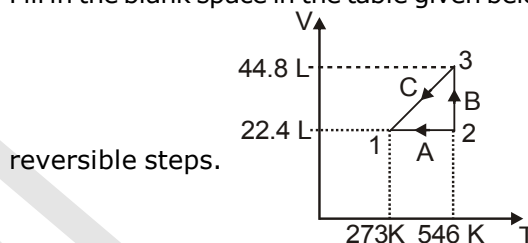
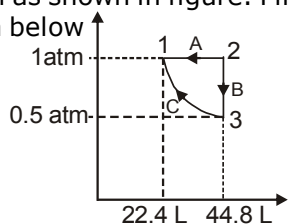


Table-1			
State	P	V	T
1			
2			
3			

Step	Name of process	q	w	ΔE	ΔH
A					
B					
C					

Sol.

21. One mole of an ideal monoatomic gas is put through reversible path as shown in figure. Fill in the blank in the table given below



State	P	V	T
1			
2			
3			

Step	Name of process	q	w	E	H
A					
B					
C					
	cyclic				

Sol.

with T going from T_1 to T_2 .

(BC) Cooling at constant volume to bring the gas to original pressure and temperature. The steps are shown schematically in the figure shown.

(a) Calculate T_1 and T_2

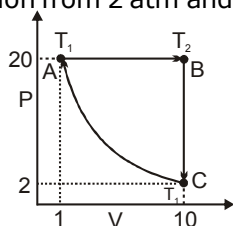
(b) Calculate ΔE , q and w in calories, for each step and for the cycle.

Sol.

22. One mole of a perfect monoatomic gas is put through a cycle consisting of the following three reversible steps.

(CA) Isothermal compression from 2 atm and 10 litres to 20 atm and 1 litre

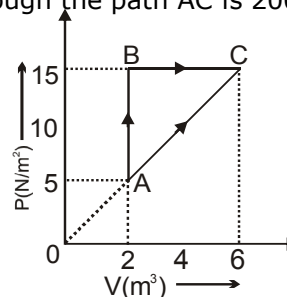
(AB) Isobaric expansion to return the gas to the original volume of 10 litres



23. The given figure shows a change of state A to state C by two paths ABC and AC for an ideal gas. Calculate the :

(a) Path along which work done is least.

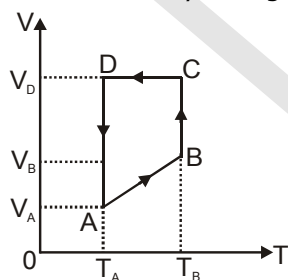
(b) Internal energy at C if the internal energy of gas at A is 10 J and amount of heat supplied to change its state to C through the path AC is 200 J.



(c) Amount of heat supplied to the gas to go from A to B, if internal energy change of gas is 10 J.

Sol.

- 24.** A monoatomic ideal gas of two moles is taken through a reversible cyclic process starting from A as shown in figure. The volume ratios are $\frac{V_B}{V_A} = 2$ and $\frac{V_D}{V_A} = 4$. If the temperature T_A at A is 27°C , calculate
- (a) The temperature of the gas at point B.
 (b) Heat absorbed or released by the gas in each



process.

- (c) The total work done by the gas during complete cycle.

Sol.

Kirchoff's Rule : Variation of Enthalpy with Temperature

25. The standard enthalpy of formation of water liquid is -285.76 kJ at 298 K . Calculate the value of $\Delta_f H^\circ$ at 373 K . The molar heat capacities at constant pressure (C_p) in the given temperature range of $\text{H}_2(\text{g})$, $\text{O}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ are respectively 38.83 , 29.16 and $75.312 \text{ JK}^{-1} \text{ mol}^{-1}$.

Sol.

26. Methane (considered to be an ideal gas) initially at 25°C and 1 bar pressure is heated at constant pressure until the volume has doubled. The variation of the molar heat capacity with absolute temperature is given by

$$C_p = 22.34 + 48.1 \times 10^{-3} T$$

where C_p in $\text{JK}^{-1} \text{mol}^{-1}$. Calculate molar (a) ΔH (b) ΔU .

Sol.

28. Oxygen is heated from 300 to 600 at a constant pressure of 1 bar. What is the increase in molar entropy? The molar heat capacity in $\text{JK}^{-1} \text{mol}^{-1}$ for the O_2 is

$$C_p = 25.5 + 13.6 \times 10^{-3} T - 42.5 \times 10^{-7} T^2$$

Sol.

Second & third law & Entropy change in thermodynamic processes

27. One mole of NaCl (s) on melting absorbed 30.5 kJ of heat and its entropy is increased by 28.8 JK^{-1} . What is the melting point of sodium chloride?

Sol.

29. A heat engine absorbs 760 kJ heat from a source at 380 K. It rejects (i) 650 kJ, (ii) 560 kJ, (iii) 504 kJ of heat to sink at 280 K. State which of these represent a reversible, an irreversible and an impossible cycle.

Sol.

30. Calculate the entropy of a substance at 600 K using the following data.

(i) Heat capacity of solid from 0 K to normal melting point 200 K $C_{p,m}(s) = 0.035 T \text{ JK}^{-1} \text{ mol}^{-1}$

(ii) Enthalpy of fusion = 7.5 kJ mol^{-1} ,

(iii) Enthalpy of vaporisation = 30 kJ mol^{-1} .

(iii) Heat capacity of liquid from 200 K to normal boiling point 300 K $C_{p,m}(l) = 60 + 0.016 T \text{ JK}^{-1} \text{ mol}^{-1}$

(iv) Heat capacity of gas from 300 K to 600 K at 1 atm $C_{p,m}(g) = 50.0 \text{ JK}^{-1} \text{ mol}^{-1}$.

Sol.

Gibb's Function

31. Calculate the free energy change at 298 K for the reaction ;

$\text{Br}_2(l) + \text{Cl}_2(g) \rightarrow 2\text{BrCl}(g)$. For the reaction $\Delta H^\circ = 29.3 \text{ kJ}$ & the entropies of $\text{Br}_2(l)$, $\text{Cl}_2(g)$ & $\text{BrCl}(g)$ at the 298 K are 152.3, 223.0, 239.7 $\text{J mol}^{-1} \text{ K}^{-1}$ respectively.
Sol.

32. Using the data given below, establish that the vaporization of $\text{CCl}_4(l)$ 298 K to produce $\text{CCl}_4(g)$ at 1atm pressure does not occur spontaneously.

Given : $\text{CCl}_4(l, 1\text{atm}) \rightarrow \text{CCl}_4(g, 1\text{atm})$;

$$\Delta S^\circ = 94.98 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$\Delta H_f^\circ(\text{CCl}_4, g) = -106.7 \text{ kJ mol}^{-1}$$

$$\& \Delta H_f^\circ(\text{CCl}_4, l) = -139.3 \text{ kJ mol}^{-1}$$

Sol.

33. Animals operate under conditions of constant pressure and most of the processes that maintain life are electrical (in a broad sense). How much energy is available for sustaining this type of muscular and nervous activity from the combustion of 1 mol of glucose molecules under standard conditions at 37°C (blood temperature)? The entropy change is +182.4 JK⁻¹ for the reaction as stated.

$$\Delta H_{\text{combustion[glucose]}} = -2808 \text{ KJ}$$

Sol.

35. From the given table answer the following questions

	CO(g)	CO ₂ (g)	H ₂ O(g)	H ₂ (g)
ΔH_{298}° (-K Cal / mole)	-26.42	-94.05	-57.8	0
ΔG_{298}° (-K Cal / mole)	-32.79	-94.24	-54.64	0
S_{298}° (-Cal / K mole)	47.3	51.1	?	31.2



(i) Calculate $\Delta_r H_{298}^{\circ}$ (ii) Calculate $\Delta_r G_{298}^{\circ}$

(iii) Calculate $\Delta_r S_{298}^{\circ}$ (iv) Calculate $\Delta_r E_{298}^{\circ}$

(v) Calculate $S_{298}^{\circ} [\text{H}_2\text{O(g)}]$

Sol.

34. At 298 K, $\Delta H_{\text{combustion}}^{\circ} (\text{sucrose}) = -5737 \text{ KJ/mol}$,

$$\Delta G_{\text{combustion}}^{\circ} (\text{sucrose}) = -6333 \text{ KJ/mol.}$$

Estimate additional non-PV work that is obtained by raising temperature to 310 K.

Assume $\Delta_r C_p = 0$ for this temperature change

Sol.

36. Calculate workdone in adiabatic compression of one mole of an ideal gas (monoatomic) from an initial pressure of 1 atm to final pressure of 2 atm. Initial temperature = 300 K.

(a) If process is carried out reversibly

(b) If process is carried out irreversible against 2 atm external pressure.

Compute the final volume reached by gas in two cases and describe the work graphically.

Sol.

37. 0.5 mole each of two ideal gases $A\left(C_v = \frac{3}{2}R\right)$ and

$B\left(C_v = \frac{5}{2}R\right)$ are taken in a container and expanded

reversibly and adiabatically from $V = 1$ L to $V = 4$ L starting from initial temperature $T = 300$ K.

Find ΔH for the process in (cal/mol).

Sol.

38. 20.0 dm³ of an ideal gas (diatomic $C_{v,m} = 5R/2$) at 673 K and 0.7 MPa expands until pressure of the gas is 0.2 MPa. Calculate q , w , ΔU and ΔH for the process if the expansion is :

(i) Isothermal and reversible

(ii) Adiabatic and reversible

(iii) Isothermal and adiabatic

(iv) Against 0.2 MPa and adiabatic

(v) Against 0.2 MPa and isothermal.

Sol.

39. One mole of a ideal monoatomic gas ($C_{v,m} = 1.5 R$) is subjected to the following sequence of steps :

(a) The gas is heated reversibly at constant pressure of 101.325 kPa from 298 K to 373 K.

(b) Next, the gas is expanded reversibly and isothermally to double its volume.

(c) Finally, the gas is cooled reversibly and adiabatically to 308 K.

Calculate q , w , ΔU and ΔH for the overall process.

Sol.

40. 2 mole of an ideal gas undergoes isothermal compression along three different paths

(i) reversible compression from $P_i = 2$ bar and $V_i = 4$ L to $P_f = 20$ bar

(ii) a single stage compression against a constant external pressure of 20 bar, and

(iii) a two stage compression consisting initially of compression against a constant external pressure of 10 bar until $P_{\text{gas}} = P_{\text{ext}}$, followed by compression against a constant pressure of 20 bar until $P_{\text{gas}} = P_{\text{ext}}$.

Calculate the work (in bar. L) for each of these processes and for which of the irreversible processes is the magnitude of the work greater ? [Given : $R = 0.08$ bar.L/mole.K]

Sol.

41. Calculate the heat of vaporisation of water per gm at 25°C and 1 atm.

Given $\Delta H_f^0 [\text{H}_2\text{O}(l)] = -285.57 \text{ kJ/mol}$

$$\Delta H_f^0 [\text{H}_2\text{O}(g)] = -241.6 \text{ kJ/mol}$$

Comment why $\Delta H_{\text{vap}}(25^\circ\text{C}) > \Delta H_{\text{vap}}(100^\circ\text{C})$

Sol.

43. (a) An ideal gas undergoes a single stage expansion against a constant opposing pressure from (P_1, V_1, T) to (P_2, V_2, T) . What is the largest mass m which mass m which can be lifted through a height h in this expansion?

(b) The system in (a) restored to initial state by a single compression. What is the smallest mass ' m ' which must fall through the height h to restore the system?

(c) What is the net mass lowered through height h in the cycle transformation in (a) and (b) ?

Sol.

42. Given: $\Delta_{\text{vap}} H$ at 373 K = 40.639 kJ mol⁻¹,

$C_p (\text{H}_2\text{O}, l) = 75.312 \text{ J K}^{-1} \text{ mol}^{-1}$,

$C_p (\text{H}_2\text{O}, g) = 33.305 \text{ J K}^{-1} \text{ mol}^{-1}$.

Pressure over 1000 ml of a liquid is gradually increases from 1 bar to 1001 bar under adiabatic conditions. If the final volume of the liquid is 990 ml, calculate ΔU and ΔH of the process, assuming linear variation of volume with pressure.

Sol.

44. Derive a mathematical expression for the work done on the surrounding when a gas that has the equation of state $PV = nRT - \frac{n^2a}{V}$ expands reversibly from V_i to V_f at constant temperature.

Sol.

46. One mole of an ideal gas is expanded isothermally at 298 K until its volume is tripled. Find the values of ΔS_{gas} and ΔS_{total} under the following conditions.

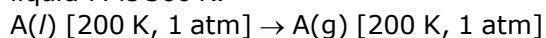
- (i) Expansion is carried out reversibly.
- (ii) Expansion is carried out irreversibly where 836.8 J of heat is less absorbed than in (i)
- (iii) Expansion is free.

Sol.

45. Calculate ΔS_f° at 298 K of ; (i) NaCl(s) , (ii) NH_4Cl (s) & diamond The values of S° of Na, Cl_2 , NaCl, NH_4Cl , N_2 , H_2 , diamond & graphite are 51, 223, 72, 95, 192, 131, 2.43 & 5.69 $\text{JK}^{-1} \text{mol}^{-1}$ respectively.

Sol.

47. The enthalpy change for vapourization of liquid 'A' at 200 K and 1 atm is 22 kJ/mol. Find out $\Delta S_{\text{vapourisation}}$ for liquid 'A' at 200 K ? The normal Boiling point of liquid 'A' is 300 K.

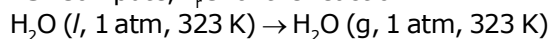


Given : $C_{p,m}(A, g) = 30 \text{ J/mol-K}$, $C_{p,m}(A, l) = 40 \text{ J/mol-K}$

Use : $\ln(3/2) = 0.405$

Sol.

49. Compute, $\Delta_r G$ for the reaction



Given that, $\Delta_{\text{vap}} H$ at 373 K = 40.639 kJ mol⁻¹, C_p

(H_2O, l) = 75.312 J K⁻¹ mol⁻¹,

$C_p(H_2O, g) = 33.305 \text{ J K}^{-1} \text{ mol}^{-1}$.

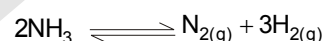
Sol.

48. Pressure of 10 moles of an ideal gas is changed from 2 atm to 1 atm against constant external pressure without change in temperature. If surrounding temperature (300 K) and pressure (1 atm) always remains constant then calculate total entropy change ($\Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$) for given process.

[Use : $\ln 2 = 0.70$ and $R = 8.0 \text{ J/mol-K}$]

Sol.

50. For the reaction



A graph is plotted between ΔG (KJ/ mole) and total pressure in atm, the equation of the graph is $P = (\Delta G)^2 - \Delta G + 3$, When Initial pressure of NH_3 is 2 atm using the above data calculate the equilibrium constant of the reaction.

EXERCISE – IV**PREVIOUS YEARS PROBLEMS****LEVEL – I****JEE MAIN**

1. The quantity required to increase the temperature of a body by 1 Kelvin is called -
(A) specific heat [AIEEE-2002]
(B) water equivalent
(C) thermal capacity
(D) molar specific heat

Sol.

2. Even Carnot engine cannot give 100% efficiency because we cannot - [AIEEE-2002]
(A) prevent radiation
(B) find ideal sources
(C) reach absolute zero temperature
(D) eliminate friction

Sol.

3. Which statement is incorrect? [AIEEE-2002]
(A) All reversible cycles have same efficiency
(B) Reversible cycle has more efficiency than an irreversible one
(C) Carnot cycle is a reversible one
(D) Carnot cycle has the maximum efficiency in all cycles

Sol.

4. "Heat cannot be itself flow from a body at lower temperature to a body at higher temperature" is a statement or consequence of - [AIEEE-2003]

- (A) Conservation of momentum
(B) Conservation of mass
(C) First law of thermodynamics
(D) Second law of thermodynamics

Sol.

5. Which of the following parameters does not characterize the thermodynamic state of matter? [AIEEE-2003]

- (A) Pressure (B) Work
(C) Volume (D) Temperature

Sol.

6. A Carnot engine takes 3×10^6 cal. of heat from a reservoir at 627°C , and gives it to a sink at 27°C . The work done by the engine is - [AIEEE-2003]

- (A) 8.4×10^6 J (B) 16.8×10^6 J
(C) Zero (D) 4.2×10^6 J

Sol.

7. In an irreversible process taking place at constant T and P and in which only pressure-volume work is being done the change in Gibbs free energy (dG) and change in entropy (dS) satisfy the criteria - **[AIEEE-2003]**

(A) $(dS)_V, E = 0, (dG)_T, p = 0$
 (B) $(dS)_V, E = 0, (dG)_T, p > 0$
 (C) $(dS)_V, E < 0, (dG)_T, p < 0$
 (D) $(dS)_V, E > 0, (dG)_T, p < 0$

Sol.

8. The internal energy change when a system goes from state A to B is 40 kJ/mole. If the system goes from A to B by a reversible path and returns to state A by an irreversible path what would be the net change in internal energy **[AIEEE-2003]**

(A) < 40 kJ (B) Zero
 (C) 40 kJ (D) > 40 kJ

Sol.

9. The correct relationship between free energy change in a reaction and the corresponding equilibrium constant K_C is - **[AIEEE-2003]**

(A) $\Delta G^\circ = RT \ln K_C$ (B) $-\Delta G^\circ = RT \ln K_C$ (C) $\Delta G = RT \ln K_C$ (D) $-\Delta G = RT \ln K_C$

Sol.

10. Which of the following statements is correct for any thermodynamic system ?

[AIEEE-2004]

(A) The internal energy changes in all processes
 (B) Internal energy and entropy are state functions
 (C) The change in entropy can never be zero
 (D) The work done in an adiabatic process is always zero

Sol.

11. An ideal gas expands in volume from $1 \times 10^{-3} \text{ m}^3$ to $1 \times 10^{-2} \text{ m}^3$ at 300 K against a constant pressure of $1 \times 10^5 \text{ Nm}^{-2}$. The work done is - **[AIEEE-2004]**

(A) -900 J (B) - 900 kJ
 (C) 2710 J (D) 900 kJ

Sol.

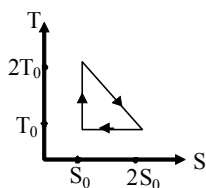
12. Which of the following is incorrect regarding the first law of thermodynamics ?

[AIEEE-2005]

(A) It is not applicable to any cyclic process
 (B) It is a restatement of the principle of conservation of energy
 (C) It introduces the concept of the internal energy
 (D) It introduces the concept of the entropy

Sol.

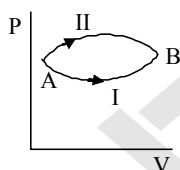
13. The temperature-entropy diagram of a reversible engine cycle is given in the figure. Its efficiency is - **[AIEEE-2005]**



- (A) 1/2 (B) 1/4 (C) 1/3 (D) 2/3

Sol.

14. A system goes from A to B via two processes I and II as shown in figure. If ΔU_1 and ΔU_2 are the changes in internal energies in the processes I and II respectively, then **[AIEEE-2005]**



- (A) $\Delta U_1 = \Delta U_2$
 (B) relation between ΔU_1 and ΔU_2 can not be determined
 (C) $\Delta U_2 > \Delta U_1$ (D) $\Delta U_2 < \Delta U_1$

Sol.

15. Consider the reaction : $\text{N}_2 + 3 \text{H}_2 \longrightarrow 2 \text{NH}_3$ carried out at constant temperature and pressure. If ΔH and ΔU are the enthalpy and internal energy changes for the reaction, which of the following expressions is true ? **[AIEEE-2005]**

- (A) $\Delta H = \Delta U$
 (B) $\Delta H = 0$
 (C) $\Delta H > \Delta U$ (D) $\Delta H < \Delta U$

Sol.

16. The work of 146 kJ is performed in order to compress one kilo mole of a gas adiabatically and in this process the temperature of the gas increases by 7°C . The gas is - **[AIEEE 2006]**
 ($R = 8.3 \text{ J mol}^{-1} \text{ K}^{-1}$) -
 (A) a mixture of monoatomic and diatomic
 (B) monoatomic
 (C) diatomic (D) triatomic

Sol.

17. An ideal gas is allowed to expand both reversibly and irreversibly in an isolated system. If T_i is the initial temperature and T_f is the final temperature, which of the following statements is correct - **[AIEEE 2006]**

- (A) $T_f > T_i$ for reversible process but $T_f = T_i$ for irreversible process
 (B) $(T_f)_{\text{rev}} = (T_f)_{\text{irrev}}$
 (C) $T_f = T_i$ for both reversible and irreversible processes
 (D) $(T_f)_{\text{irrev}} > (T_f)_{\text{rev}}$

Sol.

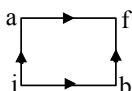
18. $(\Delta H - \Delta U)$ for the formation of carbon monoxide (CO) from its elements at 298 K is -
 ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$) [AIEEE 2006]
 (A) $1238.78 \text{ J mol}^{-1}$ (B) $-2477.57 \text{ J mol}^{-1}$
 (C) $2477.57 \text{ J mol}^{-1}$ (D) $-1238.78 \text{ J mol}^{-1}$

Sol.

19. A Carnot engine, having an efficiency of $\eta = 1/10$ as heat engine, is used as a refrigerator. If the work done on the system is 10 J, the amount of energy absorbed from the reservoir at lower temperature is [AIEEE 2007]
 (A) 99 J (B) 90 J
 (C) 1 J (D) 100 J

Sol.

20. When a system is taken from state i to state f along the path iaf, it is found that $Q = 50 \text{ cal}$ and $W = 20 \text{ cal}$. Along the path ibf $Q = 36 \text{ cal}$. W along the path ibf is - [AIEEE 2007]



- (A) 6 cal (B) 16 cal
 (C) 66 cal (D) 14 cal

Sol.

21. In conversion of lime-stone to lime, $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ the values of ΔH° and ΔS° are $+ 179.1 \text{ kJ mol}^{-1}$ and 160.2 J/K respectively at 298K and 1 bar. Assuming that ΔH° and ΔS° do not change with temperature, temperature above which conversion of limestone to lime will be spontaneous is - [AIEEE 2007]
 (A) 1008 K (B) 1200 K
 (C) 845 K (D) 1118 K

Sol.

22. Assuming that water vapour is an ideal gas, the internal energy change (ΔU) when 1 mol of water is vapourised at 1 bar pressure and 100°C , (Given : Molar enthalpy of vapourisation of water at 1 bar and 373 K = 41 kJ mol^{-1} and $R = 8.3 \text{ J mol}^{-1} \text{ K}^{-1}$) will be - [AIEEE 2007]
 (A) $4.100 \text{ kJ mol}^{-1}$ (B) $3.7904 \text{ kJ mol}^{-1}$
 (C) $37.904 \text{ kJ mol}^{-1}$ (D) $41.00 \text{ kJ mol}^{-1}$

Sol.

23. Identify the correct statement regarding a spontaneous process - [AIEEE 2007]
 (A) For a spontaneous process in an isolated system, the change in entropy is positive
 (B) Endothermic processes are never spontaneous
 (C) Exothermic processes are always spontaneous
 (D) Lowering of energy in the reaction process is the only criteria for spontaneity

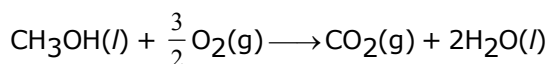
Sol.

24. Standard entropy of X_2 , Y_2 and XY_3 are 60, 40 and $50 \text{ J K}^{-1} \text{ mol}^{-1}$, respectively. For the reaction, $\frac{1}{2} X_2 + \frac{3}{2} Y_2 \rightarrow XY_3$ $\Delta H = -30 \text{ kJ}$, to be at equilibrium, the temperature will be [AIEEE 2008]

- (A) 500 K (B) 750 K
(C) 1000 K (D) 1250 K

Sol.

25. In a fuel cell methanol is used as fuel and oxygen gas is used as an oxidizer. The reaction is



At 298 K standard Gibb's energies of formation for $\text{CH}_3\text{OH}(l)$, $\text{H}_2\text{O}(l)$ and $\text{CO}_2(g)$ are -166.2 , -237.2 and $-394.4 \text{ kJ mol}^{-1}$ respectively. If standard enthalpy of combustion of methanol is -726 kJ mol^{-1} , efficiency of the fuel cell will be- [AIEEE 2009]

- (A) 87% (B) 90%
(C) 97% (D) 80%

Sol.

26. A diatomic ideal gas is used in a Carnot engine as the working substance. If during the adiabatic expansion part of the cycle the volume of the gas increases from V to $32V$, the efficiency of the engine is- [AIEEE 2010]

- (A) 0.25 (B) 0.5
(C) 0.75 (D) 0.99

Sol.

27. For a particular reversible reaction at temperature T , ΔH and ΔS were found to be both +ve. If T_e is the temperature at equilibrium, the reaction would be spontaneous when [AIEEE 2010]

- (A) $T = T_e$ (B) $T_e > T$
(C) $T > T_e$ (D) T_e is 5 times T

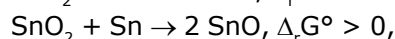
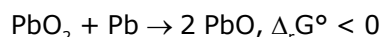
Sol.

28. The entropy change involved in the isothermal reversible expansion of 2 moles of an ideal gas from a volume of 10 dm^3 to a volume of 100 dm^3 at 27°C is : [AIEEE 2011]

- (A) $38.3 \text{ J mol}^{-1} \text{ K}^{-1}$
(B) $35.8 \text{ J mol}^{-1} \text{ K}^{-1}$
(C) $32.3 \text{ J mol}^{-1} \text{ K}^{-1}$
(D) $42.3 \text{ J mol}^{-1} \text{ K}^{-1}$

Sol.

29. In view of the signs of $\Delta_r G^\circ$ for the following reactions :



which oxidation states are more characteristic for lead and tin ? [AIEEE 2011]

- (A) For lead + 2, for tin + 2
 (B) For lead + 4, for tin + 4
 (C) For lead + 2, for tin + 4
 (D) For lead + 4, for tin + 2

Sol.

30. The incorrect expression among the following is – [AIEEE-2012]

(A) In isothermal process, $w_{\text{reversible}} = -nRT \ln$

$$\frac{V_f}{V_i}$$

(B) $\ln K = \frac{\Delta H^\circ - T\Delta S^\circ}{RT}$

(C) $K = e^{-\Delta G^\circ/RT}$

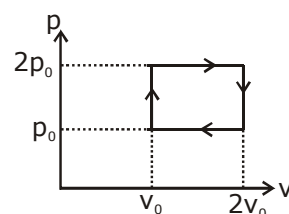
(D) $\frac{\Delta G_{\text{system}}}{\Delta S_{\text{total}}} = -T$

Sol.

31. A piston filled with 0.04 mol of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C. As it does so, it absorbs 208 J of heat. The values of q and w for the process will be: ($R = 3.314 \text{ J/mol K}$) ($\ln 7.5 = 2.01$) [AIEEE-2013]

- (A) $q = +208 \text{ J}$, $w = +208 \text{ J}$
 (B) $q = +208 \text{ J}$, $w = -208 \text{ J}$
 (C) $q = -208 \text{ J}$, $w = -208 \text{ J}$
 (D) $q = -208 \text{ J}$, $w = +208 \text{ J}$

Sol.



32.

The above p - v diagram represents the thermodynamic cycle of an engine, operating with an ideal monoatomic gas. The amount of heat, extracted from the source in a single cycle is: [AIEEE-2013]

- (A) $\left(\frac{11}{2}\right)p_0v_0$ (B) $4p_0v_0$
 (C) p_0v_0 (D) $\left(\frac{13}{2}\right)p_0v_0$

Sol.

LEVEL – II

JEE ADVANCED

1. A sample of argon gas at 1 atm pressure and 27° expands reversibly and adiabatically from 1.25 dm³ to 2.50 dm³. Calculate the enthalpy change in this process. $C_{v,m}$ for argon is 12.48 JK⁻¹ mol⁻¹.

Sol.

[JEE 2000]

2. Which of the following statement is false ?

- (A) Work is a state function
- (B) Temperature is a state function
- (C) Change of state is completely defined when initial and final states are specified.
- (D) Work appears at the boundary of the system

Sol.

[JEE 2001]

3. Show that the reaction $\text{CO(g)} + \frac{1}{2} \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$ at 300 K is spontaneous and exothermic, when the standard entropy is $-0.094 \text{ kJ mol}^{-1}\text{K}^{-1}$. The standard Gibbs free energies of formation for CO_2 and CO are -394.4 and $-137.2 \text{ kJ mol}^{-1}$, respectively.

Sol.

[JEE 2001]

4. Two moles of a perfect gas undergoes the following processes : [JEE 2002]

- (a) a reversible isobaric expansion from (1.0 atm, 20.0 L) to (1.0 atm, 40.0 L) ;
- (b) a reversible isochoric change of state from (1.0 atm, 40.0 L) to (0.5 atm, 40.0 L) ;
- (c) a reversible isothermal compression from (0.5 atm, 40.0 L) to (1.0 atm, 20.0 L) ;
- (i) Sketch with labels each of the processes on the same P-V diagram.
- (ii) Calculate the total work (w) and the total heat change (q) involved in the above processes.
- (iii) What will be the values of ΔU , ΔH and ΔS for the overall process ?

Sol.

5. One mol of non-ideal gas undergoes change of state (2.0 atm, 3.0 L, 95 K) to (4.0 atm, 5.0 L, 245 K) with a change in internal energy (ΔU) = 30.0 L-atm. The change in enthalpy (ΔH) of the process in L-atm

- (A) 40.0 (B) 42.3 (C) 44.0
- (D) not defined, because pressure is not constant

[JEE 2002]

Sol.

6. Two mole of an ideal gas is expanded isothermally and reversibly from 1 litre to 10 litre at 300 K. The enthalpy change (in kJ) for the process is

(A) 11.4 kJ (B) -11.4 kJ (C) 0 kJ (D) 4.8 kJ

Sol. [JEE 2004]

7. The enthalpy of vapourization of a liquid is 30 kJ mol⁻¹ and entropy of vapourization is 75 J mol⁻¹ K. The boiling point of the liquid at 1 atm is

(A) 250 K (B) 400 K (C) 450 K (D) 600 K

Sol. [JEE 2004]

8. One mole of a liquid (1 bar, 100 ml) is taken in an adiabatic container and the pressure increases steeply to 100 bar. Then at a constant pressure of 100 bar, volume decreases by 1 ml. Find ΔU and ΔH

Sol. [JEE 2004]

9. One mole of monoatomic ideal gas expands adiabatically at initial temp. T against a constant external pressure of 1 atm from one litre to two litre. Find out the final temp. ($R = 0.0821$ litre. atm K⁻¹ mol⁻¹):

(A) T (B) $\frac{T}{(2)^{5/3-1}}$ (C) $T - \frac{2}{3 \times 0.0821}$ (D) $T + \frac{2}{3 \times 0.0821}$

Sol. [JEE 2005]

10. A process $A \rightarrow B$ is difficult to occur directly instead it takes place in the three successive steps.

$\Delta S (A \rightarrow C) = 50$ e.u.

$\Delta S (C \rightarrow D) = 30$ e.u.

$\Delta S (B \rightarrow D) = 20$ e.u. where e.u. is entropy unit.

Then the entropy change for the process $\Delta S (A \rightarrow B)$ is:

(A) +100 e.u.

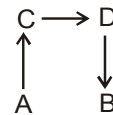
(B) -60 e.u.

(C) -100 e.u.

(D) +60 e.u.

Sol.

[JEE 2006]



11. The molar heat capacity of a monoatomic gas for which the ratio of pressure and volume is one.

- (A) $4/2 R$ (B) $3/2 R$ (C) $5/2 R$ (D) zero

Sol. [JEE 2006]

12. For the reaction.



In one litre vessel at 500 K the initial pressure is 70 atm and after the reaction it becomes 40 atm at constant volume of one litre. Calculate change in internal energy. All the above gases show significant deviation from ideal behaviour. (1 L atm = 0.1 kJ)

Sol. [JEE 2006]

13. For the process $\text{H}_2\text{O(l)} (1 \text{ bar}, 373 \text{ K}) \rightarrow \text{H}_2\text{O(g)} (1 \text{ bar}, 373 \text{ K})$, the correct set of thermodynamic parameters is

- (A) $\Delta G = 0, \Delta S = +ve$ (B) $\Delta G = 0, \Delta S = -ve$
(C) $\Delta G = +ve, \Delta S = 0$ (D) $\Delta G = -ve, \Delta S = +ve$

Sol. [JEE 2007]

14. Statement-I : There is a natural asymmetry between converting work to heat and converting heat to work.

Statement-II : No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion into work.

- (A) **Statement-I** is True, **Statement-II** is True, **Statement-II** is a correct explanation for **Statement-I**
(B) **Statement-I** is True, **Statement-II** is True, **Statement-II** is NOT a correct explanation for **Statement-I**
(C) **Statement-I** is True, **Statement-II** is False
(D) **Statement-I** is False, **Statement-II** is True

Sol. [JEE 2008]

15. Among the following, the state function(s) is (are)

(A) Internal energy [JEE 2009]

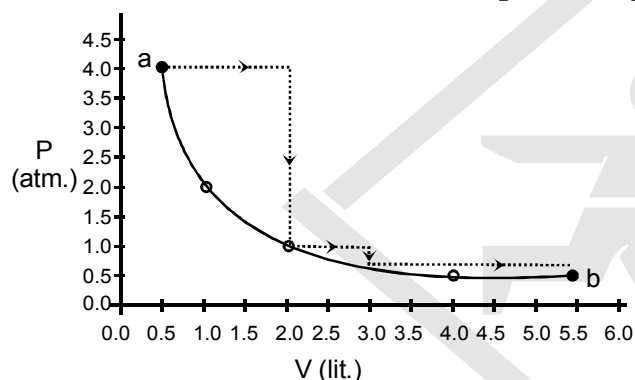
(B) Irreversible expansion work

(C) Reversible expansion (D) Molar enthalpy

Sol.

16. One mole of an ideal gas is taken from a to b along two paths denoted by the solid and the dashed lines as shown in the graph below. If the work done along the solid line path is w_s and that along the dotted line path is w_d , then integer closest to the ratio w_d/w_s is

[JEE 2010]



Sol.

17. Match the transformations in **Column-I** with appropriate options in **Column-II**. [JEE 2011]

Column-I

Column-II

(A) $\text{CO}_2(\text{s}) \rightarrow \text{CO}_2(\text{g})$

(P) Phase transition

(B) $\text{CaCO}_3(\text{s}) \rightarrow \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$

(Q) allotropic change

(C) $2\text{H}^\bullet \rightarrow \text{H}_2(\text{g})$

(R) ΔH is positive

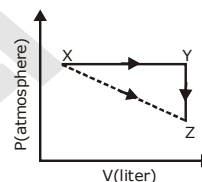
(D) $\text{P}_{(\text{white.solid})} \rightarrow \text{P}_{(\text{red, solid})}$

(S) ΔS is positive

(T) ΔS is negative

Sol.

18. For an ideal gas, consider only P-V work in going from a initial state **X** to the final state **Z**. The final state **Z** can be reached by either of the two paths shown in the figure. Which of the following choice (s) is (are) correct? [take ΔS as change in entropy and w as work done] [JEE 2012]

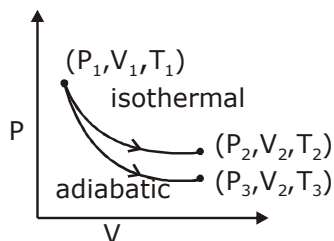


(A) $\Delta S_{x \rightarrow z} = \Delta S_{x \rightarrow y} + \Delta S_{y \rightarrow z}$ (B) $w_{x \rightarrow z} = w_{x \rightarrow y} + w_{y \rightarrow z}$

(C) $w_{x \rightarrow y \rightarrow z} = w_{x \rightarrow y}$ (D) $\Delta S_{x \rightarrow y \rightarrow z} = \Delta S_{x \rightarrow y}$

Sol.

19. The reversible expansion of an ideal gas under adiabatic and isothermal conditions is shown in the figure. Which of the following statement(s) is are correct? [JEE 2012]



- (A) $T_1 = T_2$ (B) $T_3 > T_1$
 (C) $w_{\text{isothermal}} > w_{\text{adiabatic}}$
 (D) $\Delta U_{\text{isothermal}} > \Delta U_{\text{adiabatic}}$

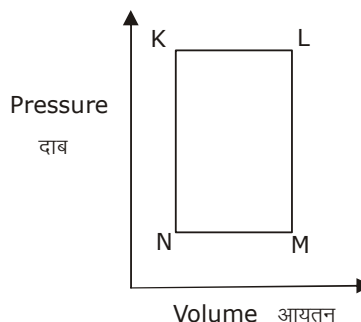
Sol.

20. Benzene and naphthalene form an ideal solution at room temperature. For this process the true statement(s) is (are) [JEE 2013]
 (A) ΔG is positive (B) ΔS_{system} is positive
 (C) $\Delta S_{\text{surrounding}} = 0$ (D) $\Delta H = 0$

Sol.

Paragraph for Questions 21 and 22

A fixed 'm' of a gas is subjected to transformation of states from K to L M to N and back to K as shown in the figure



[JEE 2013]

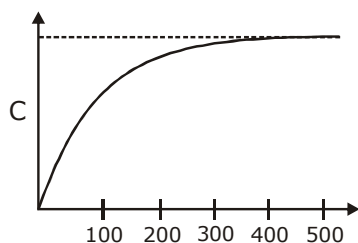
21. The succeeding operations that enable this transformation of states are
 (A) Heating, cooling, heating, cooling
 (B) Heating, cooling, cooling, heating
 (C) Cooling, heating, cooling, heating
 (D) Cooling, heating, heating, cooling

Sol.

22. The pair of isochoric processes among the transformation of states is
 (A) K to L and L to M
 (B) L to M and N to K
 (C) L to M and M to N
 (D) M to N and N to K

Sol.

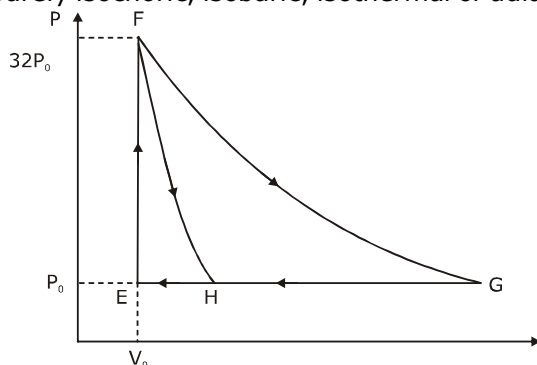
23. The figure below shows the variation of specific heat capacity (C) of a solid as a function of temperature (T). The temperature is increased continuously from 0 to 500 K at a constant rate. Ignoring any volume change, the following statement(s) is (are) correct to a reasonable approximation.



- (A) the rate at which heat is absorbed in the range 0-100 K varies linearly with temperature T .
 (B) heat absorbed in increasing the temperature from 0-100 K is less than the heat required for increasing the temperature from 400-500 K.
 (C) there is no change in the rate of heat absorption in the range 400-500 K.
 (D) the rate of heat absorption increases in the range 200-300 K

Sol.

24. One mole of a monatomic ideal gas is taken along two cyclic processes $E \rightarrow F \rightarrow G \rightarrow E$ and $E \rightarrow F \rightarrow H \rightarrow E$ as shown in the PV diagram. The processes involved are purely isochoric, isobaric, isothermal or adiabatic.



Match the paths in List I with the magnitudes of the work done in List II and select the correct answer using the codes given below the lists.

List I

- (P) $G \rightarrow E$
 (Q) $G \rightarrow H$
 (R) $F \rightarrow H$
 (S) $F \rightarrow G$

Codes :

	P	Q	R	S
(A)	4	3	2	1
(B)	4	3	1	2
(C)	3	1	2	4
(D)	1	3	2	4

Sol.

List II

1. $160 P_0 V_0 \ln 2$
 2. $36 P_0 V_0$
 3. $24 P_0 V_0$
 4. $31 P_0 V_0$

25. The standard enthalpies of formation of $\text{CO}_2(\text{g})$, $\text{H}_2\text{O}(\ell)$ and glucose(s) at 25°C are -400 kJ/mol , -300 kJ/mol and -1300 kJ/mol , respectively. The standard enthalpy of combustion per gram of glucose at 25°C is
 (A) $+2900 \text{ kJ}$ (B) -2900 kJ
 (C) -16.11 kJ (D) $+16.11 \text{ kJ}$

Sol.

Answers

Answer Ex-I

OBJECTIVE PROBLEMS (JEE MAIN)

- | | | | | | | | |
|-------|-------|-------|-------|-------|-------|-------|-------|
| 1. C | 2. D | 3. D | 4. B | 5. C | 6. B | 7. C | 8. A |
| 9. B | 10. C | 11. D | 12. C | 13. A | 14. C | 15. C | 16. D |
| 17. A | 18. A | 19. B | 20. C | 21. A | 22. C | 23. D | 24. C |
| 25. A | 26. C | 27. C | 28. C | 29. D | 30. C | 31. D | |

Answer Ex-II

OBJECTIVE PROBLEMS (JEE ADVANCED)

- | | | | | | | |
|--|----------|----------|----------|--|----------|----------|
| 1. A,B,D | 2. A,C | 3. B,C,D | 4. A,C,D | 5. A,C,D | 6. A,B,C | 7. A,B,D |
| 8. B,C,D | 9. A,B,D | 10. B | 11. D | 12. C | 13. C | 14. A |
| 15. C | 16. A | 17. D | 18. A | 19. B | 20. C | 21. C |
| 22. B | 23. D | 24. C | 25. B | 26. B | | |
| 27. (A) → P,R,S, (B) → Q,R,S, (C) → Q,R,S, (D) → R,S | | | | 28. (A) → S, (B) → P,R (C) → P,S, (D) → P, R | | |
| 29. (A) → P,S, (B) → P,R,S, (C) → Q, (D) → R,S | | | | 30. (A) → Q, (B) → P,S, (C) → P,S, (D) → S | | |
| 31. (A) → P,S,R (B) → PR, (C) → P, (D) → Q,R,S | | | | | | |

Answer Ex-III

SUBJECTIVE PROBLEMS (JEE ADVANCED)

- | | |
|--|--|
| 1. (i) w, (ii) -w, (iii) -w, (iv) w, (v) -w | 2. $q = -65 \text{ J}$; $w = 20 \text{ J}$; $\Delta E = -45 \text{ J}$ |
| 3. -0.3024 kJ | 4. (a) 0.47 gm , (b) 0.47 kg |
| 5. $\Delta E = 75.11 \text{ kJ}$ | 6. $\Delta E = 0.993 \text{ kcal}$, $\Delta H = 1 \text{ kcal}$ |
| 7. -741.5 kJ | 8. $\Delta H \cong \Delta E = 1440 \text{ calories}$ |
| 9. -10 J | 10. $q = 177.9 \text{ kJ}$, $w = -2.5 \text{ kJ}$; $\Delta E = 175.4 \text{ kJ}$ |
| 11. $\Delta E = -39.03 \text{ KJ/mole}$; $q = -36.5 \text{ kJ}$; $w = -2.53 \text{ kJ}$ | 12. $\Delta U = w = -1247.1$; $\Delta H = -1745.94 \text{ J}$ |
| 13. (i) yes (ii) $w = 0$; $q = \Delta E = 6000 \text{ J}$; $\Delta H = 9325.6 \text{ J}$ | 14. -1.683 kJ |
| 15. $T_2 = 100 \text{ K}$; $w = 5.016 \text{ KJ}$ | 16. $q = 0$; $w = \Delta U = 4.12 \text{ KJ}$; $\Delta H = 5.37 \text{ KJ}$; $V_f = 11.8 \text{ dm}^3$; $P = 5.21 \text{ atm}$ |
| 17. $C_{v,m} = 31.6 \text{ JK}^{-1}\text{mol}^{-1}$ | 18. $w = -3.988 \text{ kJ}$ |

19. $w = -P_0 V_0$; $q_{CA} = -\frac{5}{2} P^\circ V^\circ$; $q_{AB} = 3P^\circ V^\circ$; $q_{BC} = \frac{1}{2} P^\circ V^\circ T_{\max} = \frac{25}{8} \left(\frac{P^\circ V^\circ}{R} \right)$

20.

Table - 1			
State	P	V	T
1	1 atm	22.4	273
2	2 atm	22.4	546
3	1 atm	44.8	546

Step	Name of process	q	w	ΔE	ΔH
A	Isochoric	$3/2 R(273)$	0	$3/2 R(273)$	$5/2 R(273)$
B	Isothermal	$546 R \ln 2$	$-546 R \ln 2$	0	0
C	Isobaric	$-5/2 R(273)$	$R(273)$	$-3/2 R(273)$	$-5/2 R(273)$

21.

State	P	V	T
1	1 atm	22.4	273
2	1	44.8	546
3	0.5	44.8	273

Step	Name of process	q	w	ΔE	ΔH
A	Isobaric	$5/2 R(273)$	$-R(273)$	$3/2 R(273)$	$5/2 R(273)$
B	Isochoric	$-3/2 R(273)$	0	$-3/2 R(273)$	$-5/2 R(273)$
C	Isothermal	$-273 R \ln 2$	$273 R \ln 2$	0	0
	Cyclic	$R(273) - 273 R \ln 2$	$-R(273) - R \ln 2$	0	0

22. (a) $T_1 = 243.60 \text{ K}$; $T_2 = 2436.0 \text{ K}$, (b) $\Delta E = 0$; $q = -w = +3262.88 \text{ cal}$

23. (a) AC, (b) 170 J, (c) 10 J

24. (a) 600 K, (b) $q_{AB} = 3000 \text{ cal}$; $q_{BC} = 1663 \text{ cal}$; $q_{CD} = -1800 \text{ cal}$; $q_{DA} = -1663 \text{ cal}$; Total $q = 1200 \text{ cal}$,
(c) $w = -1200 \text{ cal}$

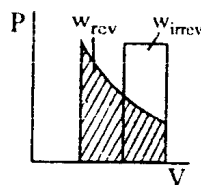
25. $\Delta H^\circ_{373}(\text{H}_2\text{O}(l)) = -284.11 \text{ kJ}$ 26. (a) $13.064 \text{ kJ mol}^{-1}$, (b) $10.587 \text{ kJ mol}^{-1}$

27. $T = 1059 \text{ K}$

28. $21.18 \text{ JK}^{-1} \text{ mol}^{-1}$

29. (i) irreversible, (ii) reversible, (iii) impossible
30. $205.08 \text{ JK}^{-1} \text{ mol}^{-1}$
31. -1721.8 J 32. $\Delta G^\circ = 4.3 \text{ kJ mol}^{-1}$ 33. -2864.5 KJ
34. 24 kJ/mol
35. (i) -9.83 Kcal/mole , (ii) -6.81 Kcal/mole , (iii) -10.13 Cal/Kmole , (iv) -9.83 Kcal/mole
(v) $+45.13 \text{ Cal/Kmole}$

36. (a) $T_2 = 395.8$; $V_2 = 16.24 \text{ L}$; $w_{\text{rev}} = 1194.72 \text{ J}$,
(b) $V_2' = 17.24 \text{ L}$; $T_2' = 420 \text{ K}$, $w_{\text{irrev}} = 1496.52 \text{ J}$



37. -900 calories
38. (i) $q = -w = 17.54 \text{ kJ}$, $\Delta U = 0$ and $\Delta H = 0$; (ii) $q = 0$, $w = \Delta U = -10.536 \text{ kJ}$ and $\Delta H = -14.75 \text{ kJ}$
(iii) $q = 0$, $w = 0$, $\Delta U = 0$ and $\Delta H = 0$ (iv) $q = 0$; $\Delta U = w = -7.14 \text{ KJ}$; $\Delta H = -9.996 \text{ KJ}$,
(v) $q = -w = 10.0 \text{ KJ}$, $\Delta U = \Delta H = 0$
39. (a) $q = \Delta H = 1558.88$, $\Delta U = 935.33$; $w = -P(\Delta U) = -623.55 \text{ J mol}^{-1}$
(b) $w = -2149.7$; ΔU & $\Delta H = 0$, $q = -w$
(c) $q = 0$, $w = -810.62$, $\Delta H = -1351.03 \text{ Jmol}^{-1}$
for overall process $q = 3708.59$; $w = -3583.88$, $\Delta U = 124.71$; $\Delta H = 207.85$
40. (i) 18.424 bar. L ; (ii) 72 bar. L ; (iii) 40 bar L .
Magnitude of work is maximum in single stage compression
41. $\Delta H_{\text{vap}}(25^\circ\text{C}) = 43.97 \text{ kJ/mol} = 2.433 \text{ kJ/gm}$, $\Delta H_{\text{vap.}}(100^\circ\text{C}) = 40.62 \text{ KJ/mol}$ (given)
42. $\Delta U = 501 \text{ J}$; $\Delta H = 99.5 \text{ kJ}$

43. (a) $m = \frac{nRT}{gh} \left(1 - \frac{P_2}{P_1} \right)$, (b) $m' = \frac{nRT}{gh} \left(\frac{P_1}{P_2} - 1 \right)$ (c) $m' - m = \frac{nRT}{gh} \left(\frac{(P_1 - P_2)^2}{P_1 P_2} \right)$

44. $w = -nRT \ln \frac{V_f}{V_i} - n^2 a \left(\frac{1}{V_f} - \frac{1}{V_i} \right)$

50. 1.68

Answer Ex-IV**PREVIOUS YEARS PROBLEMS****LEVEL – I****JEE MAIN**

- | | | | | | | | |
|-------|-------|-------|-------|-------|-------|-------|-------|
| 1. C | 2. C | 3. A | 4. D | 5. B | 6. A | 7. D | 8. B |
| 9. B | 10. B | 11. A | 12. A | 13. C | 14. A | 15. D | 16. C |
| 17. D | 18. A | 19. B | 20. A | 21. D | 22. C | 23. A | 24. B |
| 25. C | 26. C | 27. C | 28. A | 29. C | 30. B | 31. B | 32. D |

LEVEL – II**JEE ADVANCED**

- | | | |
|--|-------------|--|
| 1. $\Delta H \approx -115 \text{ J}$ | 2. A | 3. $\Delta H^\circ = -285.4 \text{ kJ/mol}$, $\Delta G^\circ = -257.2 \text{ kJ/mol}$ |
| 4. (ii) $-w = q = 620.77 \text{ J}$, (iii) $\Delta H = 0$, $\Delta U = 0$, $\Delta S = 0$ | 5. C | 6. C |
| 8. $\Delta U = 0.1 \text{ litre atm}$, $\Delta H = 9.9 \text{ litre atm}$ | 9. C | 10. D |
| 13. A | 14. A | 15. A, D |
| 18. A, C | 19. A, C, D | 20. B, C, D |
| 24. A | 25. C | |
| | | 16. 2 |
| | | 17. A-PRS, B-RS, C-T, D-PQT |
| | | 21. C |
| | | 22. B |
| | | 23. ABCD |
| | | 7. B |
| | | 11. A |
| | | 12. -557 kJ/mol |

THERMOCHEMISTRY

Thermochemistry is the branch of physical chemistry which deals with the thermal or heat changes caused by chemical reactions.

SPECIFIC HEAT (S)

Amount of energy required to raise the temp by 1° C of 1 gm of a substance.

Unit → J/kg-K

HEAT CAPACITY (ms)

The amount of heat required to raise the temperature by 1°C or 1K of a given amount of a substance.

Units → J/K

Total heat given to increase the temperature by Δt .

$$q = ms\Delta t$$

MOLAR HEAT CAPACITY (C_m)

The amount of heat required to raise the temp by 1° of 1 mole of a substance.

CLASSIFICATION OF MOLAR HEAT CAPACITY

(A) Molar heat capacity at constant pressure (C_{p,m})

(B) Molar heat capacity at constant volume (C_{v,m})

Relation between C_p and C_v

$$C_p - C_v = R \quad (\text{Mayor's formula})$$

$$\frac{C_p}{C_v} = \gamma \quad (\text{Poisson's Ratio})$$

RULES FOR THERMOCHEMICAL EQUATION

(1) It is necessary to mention physical state of all reactants and products.

(2) $A \rightarrow B, \Delta H = H_B - H_A$

If $A \rightarrow B + x \text{ kJ/mole}$

$\Delta H < 0 \Rightarrow$ (Exothermic reaction)

$\Delta H = -x \text{ kJ/mole}$

If $A + x \text{ kJ/mole} \rightarrow B$

$\Delta H > 0 \Rightarrow$ (Endothermic reaction)

$\Delta H = +x \text{ kJ/mole}$

(3) After reversing a thermochemical eqⁿ then sign of enthalpy also get changed.

e.g. $A_{(g)} + B_{(g)} \rightarrow C_{(g)} + D_{(g)}, \Delta H = x \text{ kJ}$

$C_{(g)} + D_{(g)} \rightarrow A_{(g)} + B_{(g)}, \Delta H = -x \text{ kJ}$

(4) When two reactions are added their enthalpies are also get added with their sign.

e.g.

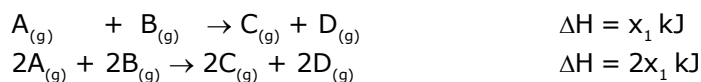
$A_{(g)} + B_{(g)} \rightarrow C_{(g)} + D_{(g)} \quad \Delta H = x_1 \text{ kJ}$

$C_{(g)} + E_{(g)} \rightarrow F_{(g)} \quad \Delta H = -x_2 \text{ kJ}$

$A_{(g)} + B_{(g)} + E_{(g)} \rightarrow D_{(g)} + F_{(g)}, \Delta H = x_1 - x_2$

- (5) If a thermochemical equation is multiplied by a number then ΔH is multiplied by the same number.

e.g.



INTENSIVE PROPERTY

The property which does not depend upon the mass of substance is called intensive property.

e.g. density, refractive index, specific heat, etc.

EXTENSIVE PROPERTY

Mass dependent properties are called extensive properties

e.g. ΔH , ΔS , ΔG , V , U , Resistance, Number of moles etc.

- * Two extensive property can be added
 - * Ratio of two extensive properties is Intensive.
 - * Intensive properties can not be added directly.
- e.g. We can not add the density of two liquids to get the density of the final mixture of the two.

ENTHALPY (H)

$$H = U + PV$$



Internal energy

$$\Delta H = \Delta U + \Delta(PV) = \Delta U + (P_2V_2 - P_1V_1)$$

- (i) At constant Pressure, $\Delta H = \Delta U + P\Delta V$

- (ii) At Constant Volume, $\Delta H = \Delta U + V\Delta P$

- * Enthalpy of ideal gas is function of temperature only.
- * Enthalpy is always defined at constant temperature and it varies with variation in temperature.

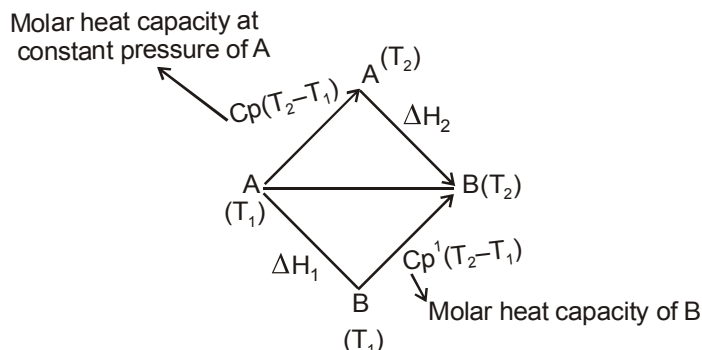
$$\begin{array}{lcl} H = U + PV \\ = U + nRT \\ \Rightarrow \Delta H = \Delta n C_p T \\ \Delta H = \Delta E + \Delta n RT \\ \downarrow \qquad \qquad \downarrow \\ \text{Heat at a constant pressure} \quad \text{heat at a constant Volume} \end{array}$$

Where Δn_g = no. of moles of gaseous product - no. of moles of gaseous reactant.

KIRCHOFF'S EQUATION

This gives the relation between enthalpy and temperature.

- * Physical state is changed at constant temperature.



According to Hess' Law

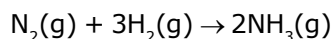
$$\begin{aligned}\Delta H_2 + C_p(T_2 - T_1) &= \Delta H_1 + C_{p1}(T_2 - T_1) \\ \Delta H_2 - \Delta H_1 &= (C_{p1} - C_p)(T_2 - T_1) \\ &= \Delta C_p(T_2 - T_1)\end{aligned}$$

$$\Rightarrow \Delta C_p = \frac{\Delta H_2 - \Delta H_1}{T_2 - T_1}$$

Where

ΔC_p = Molar heat capacity of product -- Molar heat capacity of reactant

e.g.



$$\Delta C_p = 2C_p(\text{NH}_3) - C_p(\text{N}_2) - 3C_p(\text{H}_2)$$

- * If the above formula (Kirchoff's eqⁿ) is to be written for molar heat capacity at constant volume then

$$\Delta C_v = \frac{\Delta U_2 - \Delta U_1}{T_2 - T_1}$$

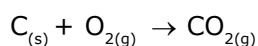
- * If ΔC_p is function of temperature

$$\Delta C_p = T^2 + T$$

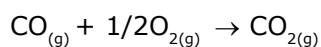
$$\text{Then } \int_{T_1}^{T_2} \Delta C_p dT = \Delta H_2 - \Delta H_1$$

HEAT OF FORMATION

Enthalpy change during the formation of 1 mole of a compound from its most stable common occurring form (also called reference states) of elements is called heat of formation.



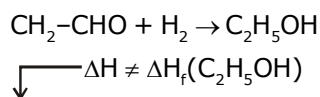
$$\Delta H = \Delta H_f(\text{CO}_2)$$



$$\Delta H \neq \Delta H_f \text{CO}_2(\text{g})$$

(because CO_2 has not been formed from its element in their most stable form)

Similarly



Heat of reaction

Element	Most stable form
H	$\text{H}_2(\text{gas})$
O	$\text{O}_2(\text{gas})$
N	$\text{N}_2(\text{gas})$
F	$\text{F}_2(\text{gas})$
Cl	$\text{Cl}_2(\text{gas})$
Br	$\text{Br}_2(\text{gas})$
I	$\text{I}_2(\text{solid})$
C	C(graphite)
P	P(white)
S	S(rhombic)

* All metal except Hg exist in solid form (reference states)

ENTHALPY AT STANDARD STATE $:-(\Delta H^\circ)$

$$T = 25^\circ\text{C} = 298 \text{ K}$$

$$P = 1 \text{ atm}$$

$$\text{Conc} = 1\text{M}$$

ΔH° = Heat of formation at standard state

If $\text{A}_{(\text{g})} + \text{B}_{(\text{g})} \rightarrow \text{C}_{(\text{g})} + \text{D}_{(\text{g})}$ is any reaction, Heat of reaction for any thermochemical equation can be written as

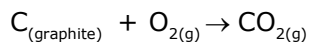
$$\Delta H^\circ = \Delta H_f^\circ(\text{product}) - \Delta H_f^\circ(\text{Reactant})$$

If we use the above concept for the above given reaction then

$$\Delta H^\circ = \Delta H_f^\circ(\text{C}) + \Delta H_f^\circ(\text{D}) - \Delta H_f^\circ(\text{A}) - \Delta H_f^\circ(\text{B})$$

Assumption :-

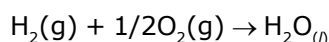
The heat of formation of most stable form of an element is taken as zero.



$$\Delta H^\circ = \Delta H_f^\circ(\text{CO}_2) - \Delta H_f^\circ\text{C}_{(\text{s})} - \Delta H_f^\circ(\text{O}_2)(\text{g})$$

$$\Rightarrow \Delta H^\circ = \Delta H_f^\circ(\text{CO}_2) \quad (\text{As } \Delta H_f^\circ\text{C}_{(\text{s})} = 0 \text{ and } \Delta H_f^\circ\text{O}_2(\text{g}) = 0)$$

Another example can be taken as

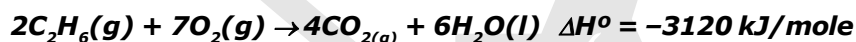


$$\Delta H^\circ = \Delta H_f^\circ(\text{H}_2\text{O}) - \Delta H_f^\circ(\text{H}_2) - 1/2 \Delta H_f^\circ(\text{O}_2)$$



$$\Delta H^\circ = \Delta H_f^\circ(\text{H}_2\text{O})$$

Ex.1 From the following data,



Calculate the standard enthalpy of formation of

$\text{C}_2\text{H}_6(\text{g})$ (in kJ/mole)

Sol. From eqⁿ(1) $\Delta H_f^\circ(\text{CO}_2) = -393.5 \text{ kJ/mole}$

From eqⁿ(2) $\Delta H_f^\circ(\text{H}_2\text{O}) = -286 \text{ kJ/mole}$

From eqⁿ (3) $\Delta_r H^\circ = 4 \Delta H_f^\circ(\text{CO}_2) + 6 \Delta H_f^\circ(\text{H}_2\text{O}) - 2 \times \Delta H_f^\circ(\text{C}_2\text{H}_6) - 7 \times \Delta H_f^\circ\text{O}_2(\text{g})$

$$-3120 = 4 \times (-393.5) + 6 \times (-286) - 2 \times \Delta H_f^\circ(\text{C}_2\text{H}_6) \quad (\text{As } \Delta H_f^\circ \text{O}_2(\text{g}) = 0)$$

$$\Rightarrow -3120 = -1574 - 1716 - 2 \times \Delta H_f^\circ(\text{C}_2\text{H}_6)$$

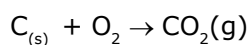
$$\Rightarrow -3120 + 3290 = -2 \times \Delta H_f^\circ(\text{C}_2\text{H}_6)$$

$$\Rightarrow 170 = -2 \times \Delta H_f^\circ(\text{C}_2\text{H}_6)$$

$$\Rightarrow \Delta H_f^\circ = -85 \text{ kJ/mole}$$

HEAT OF COMBUSTION

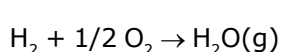
It is the enthalpy change (always -ve) when One mole of the substance undergo complete combustion.



$$\Delta H^\circ = \Delta H_c^\circ \text{C}(s) = \Delta H_f^\circ(\text{CO}_2) - \Delta H_f^\circ \text{C}(s) - \Delta H_f^\circ(\text{O}_2)$$

$$\Delta H^\circ = \Delta H_c^\circ \text{C}(s) = \Delta H_f^\circ(\text{CO}_2)$$

Other example

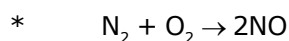


$$\Delta H^\circ = \Delta H_c^\circ (\text{H}_2) = \Delta H_f^\circ (\text{H}_2\text{O}) - \Delta H_f^\circ(\text{H}_2) - 1/2\Delta H_f^\circ (\text{O}_2)$$

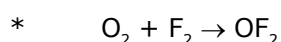
$$\Delta H^\circ = \Delta H_f^\circ (\text{H}_2\text{O}) = \Delta H_f^\circ (\text{H}_2\text{O})$$

Note :-

Heat of combustion is always exothermic



(It is an endothermic reaction)



(Since O has normally tendency to accept electron and opposite is happening above hence reaction is is considered endothermic)

* Heat of reaction for any thermochemical equation can be written as (in form of heat of combustion)

$$\Delta H_r^\circ = \text{Heat of combustion of reactant} - \text{Heat of combustion of reactant} .$$

$$\Delta H_r^\circ = \Delta H_c^\circ (\text{Reactant}) - \Delta H_c^\circ (\text{Product})$$

Ex.2 The enthalpy change for the reaction

$\text{C}_3\text{H}_8(g) + \text{H}_2(g) \rightarrow \text{C}_2\text{H}_6(g) + \text{CH}_4(g)$ at 25°C is -55.7 kJ/mole calculate the enthalpy of combustion of $\text{C}_2\text{H}_6(g)$. The enthalpy of combustion of H_2 and CH_4 are -285.8 and -890.0 kJ/mole respectively. Enthalpy of combustion of propane is -2220 kJmol^{-1} .

Sol. As we know any thermochemical eqⁿ can be written in terms of heat of combustion as follows

$$\Delta H_r^\circ = \Delta H_c^\circ (\text{Reactant}) - \Delta H_c^\circ (\text{Product})$$

$$\Delta H_r^\circ = \Delta H_c^\circ (\text{C}_3\text{H}_8) + \Delta H_c^\circ (\text{H}_2) - \{ \Delta H_c^\circ(\text{C}_2\text{H}_6) + \Delta H_c^\circ(\text{CH}_4) \}$$

$$-55.7 = (-2220 - 285.8) - \{ -890 + \Delta H_c^\circ(\text{C}_2\text{H}_6) \}$$

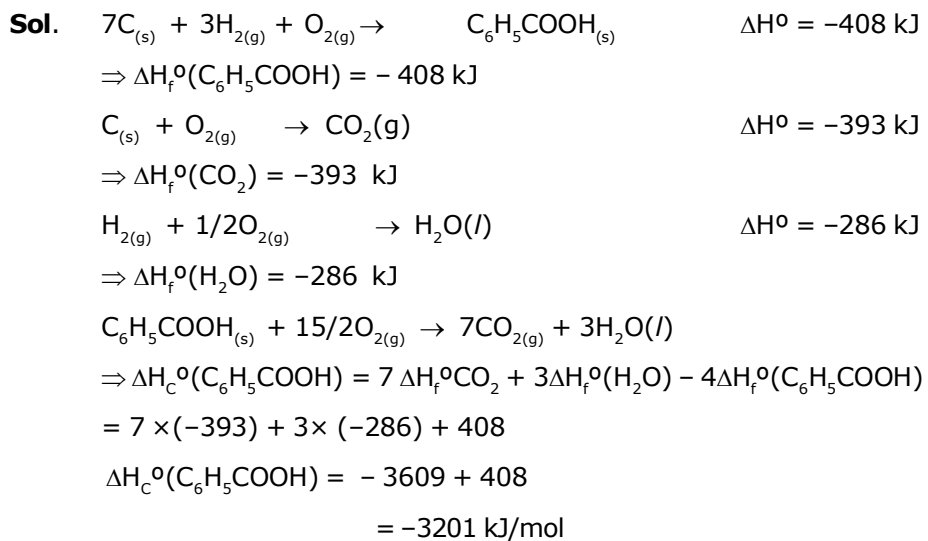
$$\Rightarrow \Delta H_c^\circ(\text{C}_2\text{H}_6) (g) = -1560.1 \text{ kJmol}^{-1}$$

Problems Based on Both HOC and HOF :

Ex.3 At 300K , the standard enthalpies of formation of $\text{C}_6\text{H}_5\text{COOH}_{(s)}$, $\text{CO}_2(g)$ and $\text{H}_2\text{O}(l)$ are -408 , -393 and -286 kJmol^{-1} respectively. Calculate the enthalpy of combustion of benzoic acid at

(i) constant pressure

(ii) constant volume.



\Rightarrow enthalpy of combustion at constant pressure = $-3201 \text{ kJ mol}^{-1}$

Also

$$\Delta H = \Delta U + \Delta n gRT$$

$$-3201 = \Delta U + (-0.5) \times 8.31 \times 10^{-3} \times 300$$

(As $\Delta n = 0.5$, $R = 8.314 \times 10^{-3} \text{ kJ}$)

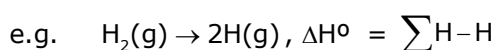
$$\Rightarrow \Delta U = -3201 + 1.2471$$

$$\Delta U = -3199.7529$$

\Rightarrow enthalpy of combustion at constant volume = -3199.7529

BOND ENERGY

It is defined for gaseous molecules. "The enthalpy change during the breaking of one mole of bond into isolated gaseous atoms is called bond energy of the compound"



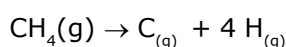
$$\Delta H^\circ = \sum \text{H-H} = 2\Delta H_f^\circ\text{H}(g) - \Delta H_f^\circ(\text{H}_2)$$

$$\Rightarrow \sum \text{H-H} = 2\Delta H_f^\circ\text{H}(g) \quad \Rightarrow \Delta H_f^\circ\text{H}(g) = \frac{\sum \text{H-H}}{2}$$

Similarly

$$\Delta H_f^\circ\text{O}(g) = \frac{\sum \text{O=O}}{2}, \Delta H_f^\circ\text{N}(g) = \frac{\sum \text{N}\equiv\text{N}}{2}$$

* Let us consider the similar bond breaking In CH_4

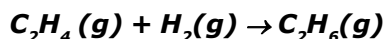


$$\Delta H = 4\sum \text{C-H} = \Delta H_f^\circ\text{C}(g) + 4\Delta H_f^\circ\text{H}(g) - \Delta H_f^\circ(\text{CH}_4)$$

** Enthalpy of reaction in terms of bond energy for a thermochemical eqⁿ can be written as

$$\Delta H_f^\circ = \text{B.E.}_{(\text{Reactant})} - \text{B.E.}_{(\text{products})}$$

Ex.4 Using the bond enthalpy data given below, calculate the enthalpy change for the reaction



Data :

Bond	C – C	C = C	C – H	H – H
Bond Enthalpy(Kg/mol)	336.81	606.68	410.87	431.79

Sol. $\Delta_r H^\circ = \sum \text{reactant} - \sum \text{product}$

$$\Delta H_r^\circ = \sum \text{C}=\text{C} + 4\sum \text{C}-\text{H} + \sum \text{H}-\text{H} - \sum \text{C}-\text{C} - 6\sum \text{C}-\text{H}$$

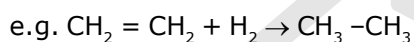
$$\Delta H_r^\circ = 606.68 + 4 \times 410.87 + 431.79 - 336.81 - 6 \times 410.87 = 2681.95 - 2802.03$$

$$\Delta H_r^\circ = -120.08 \text{ kJ/mol}$$

HEAT OF HYDROGENATION

"Enthalpy change during the addition of 1 mole of H_2 to an unsaturated compound. is called heat of hydrogenation."

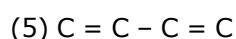
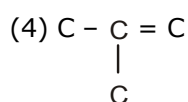
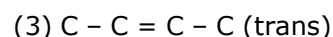
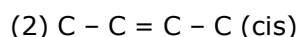
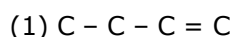
Hydrogenation is an exothermic process. of therefore heat of hydrogenaiton is always –ve.



$$\Delta H_r^\circ = \Delta H^\circ (\text{Hydrogenation of } \text{CH}_2 = \text{CH}_2)$$

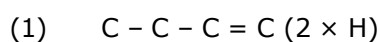


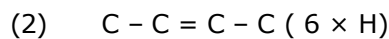
Ex.5 Compare the heat of hydrogenation of the following alkene



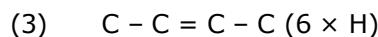
Sol. Stability of alkene $\propto \frac{1}{\text{Heat of hydrogenation}}$

The above concept is true as long as no. of double bonds are equal as heat of hydrogenation is defined for per mole of double bond. It will be certainly larger for higher number of double bonds irrespective of their stability.

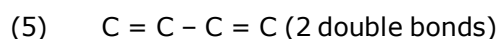




(cis)

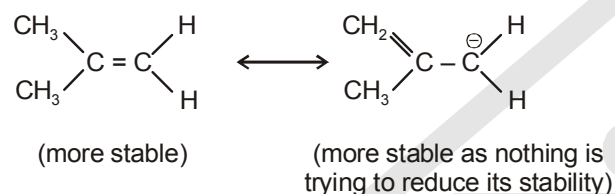
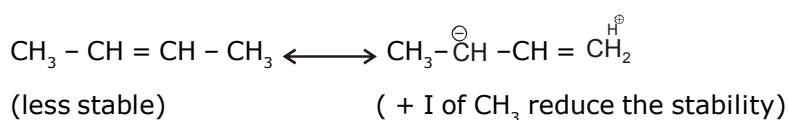


(trans)

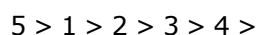


As we know trans > cis (stability)

⇒ Heat of hydrogen (trans) < Heat of hydrogenation (cis)



of therefore decreasing order of heat of hydrogenation of alkene



Ex.6 Find ΔH_f of $HCl(g)$ if bond energies of H_2 , Cl_2 and HCl are 104, 58, 103 kcal/mole respectively.

Sol. $H - Cl \rightarrow H(g) + Cl(g)$

$$\sum H - Cl = \Delta H_f^\circ H(g) + H_f^\circ Cl(g) - \Delta H_f^\circ HCl(g)$$

$$103 = \frac{1}{2} \sum H - H + \frac{1}{2} \sum Cl - Cl - \Delta H_f^\circ HCl(g)$$

$$103 = \frac{1}{2} \times 104 + \frac{1}{2} \times 58 - \Delta H_f^\circ HCl(g)$$

$$\Rightarrow \Delta H_f^\circ HCl(g) = -22 \text{ kcal/mol.}$$

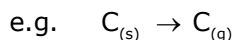
HEAT OF ATOMISATION

" When one mole of any substance is converted into gaseous atoms enthalpy change during the process is called heat of atomisation." It is always + ve.

HEAT OF SUBLIMATION

Enthalpy change during the conversion of one mole of solid to 1 mole of gaseous phase directly without undergoing into liquid phase is called enthalpy of sublimation or heat of sublimation,

It is always +ve due to endothermic nature of the process.



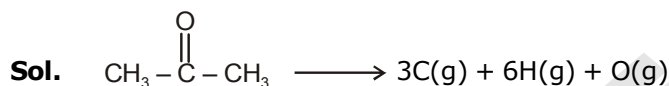
$$\Delta H^{\circ} = \Delta H_{\text{sub}}^{\circ} C(s) = \Delta H_f^{\circ} C(g) - \Delta H_f^{\circ} C(s)$$

$$\Rightarrow \Delta H_{\text{sub}}^{\circ} C(s) = \Delta H_f^{\circ} C(g)$$

$$\Rightarrow \Delta H_{\text{sub}}^{\circ} C(s) = \Delta H_f^{\circ} C(g) = \Delta H_{\text{atomisation}}^{\circ} C(g)$$

Ex.7 Using the given data, calculate enthalpy of formation of acetone(g) [All values in kJmol^{-1}]
bond enthalpy of $C-H = 413.4$, $C-C = 347.0$ ($C=O = 728.0$

$$O=O = 495.0, \quad H-H = 435.8 \quad \Delta_{\text{sub}} H \text{ of } C = 718.4$$



$$6 \sum C-H + \sum C=O + 2 \sum C-C = 3\Delta H_f^{\circ} C(g) + 6\Delta H_f^{\circ} H(g) + \Delta H_f^{\circ} O(g) - \Delta H_f^{\circ} (\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3)$$

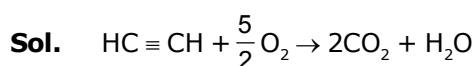
$$6 \times 413.4 + 728 + 2 \times 347 = 3 \times 718.4 + \frac{6}{2} \times 435.8 + \frac{1}{2} \times 495.0 - \Delta H_f^{\circ} (\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3)$$

$$\Rightarrow \Delta H_f^{\circ} (\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3) = -192.3 \text{ kJmol}^{-1}$$

Ex.8 The enthalpy of combustion of acetylene is 312 kcal. If enthalpy of formation of CO_2 and H_2O are -94.38 and -68.38 kcal respectively

Calculate $C \equiv C$ bond enthalpy.

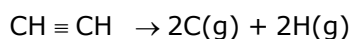
Given that enthalpy of atomisation of 150 kcal and $H-H$ bond enthalpy and $C-H$ bond enthalpy are 103 kcal and 93.64 kcal respectively.



$$\Delta H_c^{\circ} (\text{CH} \equiv \text{CH}) = 2\Delta H_f^{\circ} (\text{CO}_2) + \Delta H_f^{\circ} (\text{H}_2\text{O}) - \Delta H_f^{\circ} (\text{C}_2\text{H}_2)$$

$$-312 = 2 \times (-94.38) + (-68.38) - \Delta H_f^{\circ} (\text{C}_2\text{H}_2)$$

$$\Delta H_f^{\circ} (\text{C}_2\text{H}_2) = 54.86$$



$$\sum C \equiv C + 2 \sum C-H = 2\Delta H_f^{\circ} C(g) + 2\Delta H_f^{\circ} H(g) - \Delta H_f^{\circ} (\text{CH} \equiv \text{CH})$$

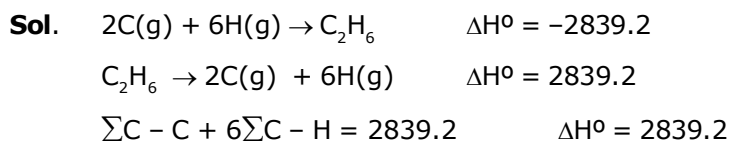
$$\sum C \equiv C + 2 \times 93.64 = 2 \times 150 + 2 \times \frac{1}{2} \times 103 - 54.86 \Rightarrow \sum C \equiv C = 160.86 \text{ kJmol}^{-1}$$

RESONANCE ENERGY

"The energy difference between resonance hybrid and most stable canonical structure is called resonance energy".

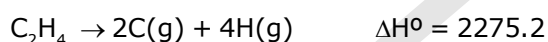
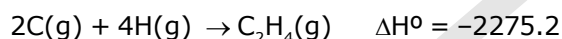
Resonance energy is generally -ve as nature of the process is exothermic.

Ex.9 *The enthalpy of formation of ethane, ethylene and benzene from the gaseous atoms are -2839.2, -2275.2 and -5506 kJmol⁻¹ respectively. Calculate the resonance energy of benzene. The bond enthalpy of C - H bond is given as equal to + 410.87 kJ/mol.*



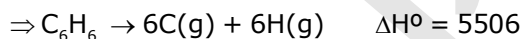
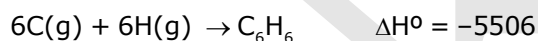
$$\sum C - C + 6 \times 410.87 = 2839.2$$

$$\Rightarrow \sum C - C = 373.98 \quad \dots (1)$$



$$\sum C = C + 4\sum C - H = 2275.2$$

$$\sum (C = C) = 631.72 \quad \dots (2)$$

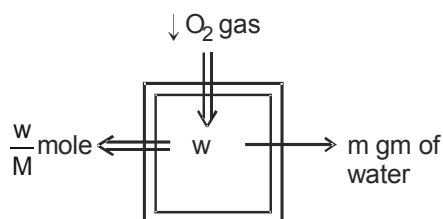


$$\Rightarrow 3\sum C = C + 3\sum C - C + 6\sum C - H + x = 5506$$

Putting all the values from eqⁿ, 1, & 2 we get $x = 23.68$

\Rightarrow Resonance energy of benzene = - 23.68 kJ/mole

BOMB CALORIMETER



$$\text{Heat evolved} = ms\Delta t + C\Delta t$$

↓

Heat capacity of container

$$\text{Heat of combustion} = - \frac{[ms\Delta t + C\Delta t]}{\left(\frac{w}{M}\right)}$$

$$= - \frac{M}{w} [ms\Delta t + C\Delta t] = - \frac{M}{w} \times \Delta t [ms + C]$$

$$= - \frac{M}{w} \times \Delta t [C' + C]$$

\downarrow \downarrow
 Heat capacity Heat capacity
 of water of container

$$\Rightarrow \Delta H = - \frac{M}{w} \times \Delta t \times C \rightarrow \text{Heat capacity of system}$$

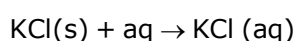
Ex.10 When 1.0 gm of fructose $C_6H_{12}O_6(s)$ is burnt in oxygen in a bomb calorimeter, the temperature of the calorimeter water increases by 1.56°C . If the heat capacity of the calorimeter and its contents is $10.0 \text{ kJ}/^\circ\text{C}$. Calculate the enthalpy of combustion of fructose at 298 K.

Sol. Heat capacity of the system

$$\begin{aligned} \Delta H_c &= \frac{-M}{w} [C \times \Delta t] \\ &= \frac{-180}{1} [10 \times 1.56] = -2808 \text{ kJ/mole} \end{aligned}$$

HEAT OF SOLUTION

Enthalpy change during the dissolution of 1 mole of salt in excess of solvent.



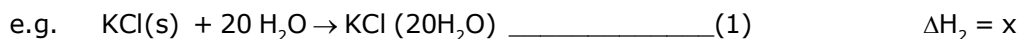
$$\Delta H^\circ = \text{Heat of sol}^n \text{ of KCl}(s)$$

Note :-

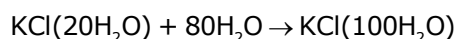
- (1) Heat of solution is always exothermic for the anhydrous form of salts which can form their hydrates.
e.g. $\text{CuSO}_4, \text{Na}_2\text{SO}_4, \text{FeSO}_4, \text{ZnSO}_4, \text{CaCl}_2, \text{LiCl}$ etc.
 $\text{CuSO}_4(s) + aq \rightarrow \text{CuSO}_4(aq) \Delta H < 0$
- (2) Heat of solution is endothermic for the hydrated form of the salt.
 $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} + aq \rightarrow \text{CuSO}_4(aq) \Delta H > 0$
- (3) Heat of solⁿ is endothermic for the salts which do not form their hydrates.
e.g. $\text{NaCl}, \text{NaNO}_3, \text{KCl}$ etc.

INTEGRAL HEAT OF SOLUTION

Enthalpy change when 1 mole of salt is dissolved in given amount of solvent.

**HEAT OF DILUTION**

Reversing the eqⁿ (1) and adding in (2)



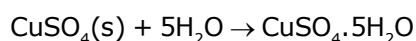
$$\Delta H = y - x$$

enthalpy change when the conc. of salt changes from one to another on the basis of dilution

$$\Rightarrow \Delta H = y - x = \text{Heat of dilution}$$

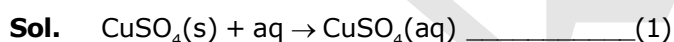
HEAT OF HYDRATION

Enthalpy change during the formation of hydrated form of salt from its anhydrous form. It is always exothermic.

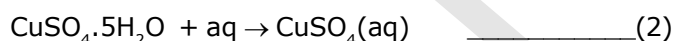


$$\Delta H = \text{Heat of hydration of CuSO}_4(\text{s})$$

Ex.11 Heat of solⁿ of $\text{CuSO}_4(\text{s})$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is 15.9 and 19.3 kJ/mol respectively. Find the heat of hydration of $\text{CuSO}_4(\text{s})$

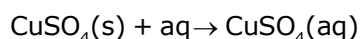


$$\Delta H = -15.9$$

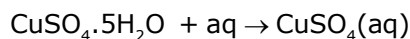


$$\Delta H = 19.3$$

Reversing eqⁿ (1) and adding (2)



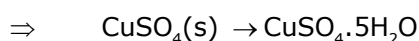
$$\Delta H = 15.9$$



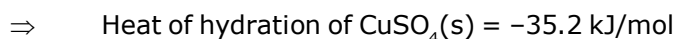
$$\Delta H = 19.3$$



$$\Delta H = 35.2$$

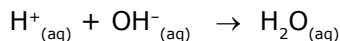
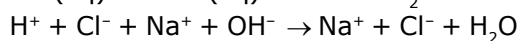
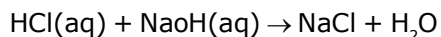


$$\Delta H = -35.2$$

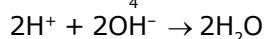
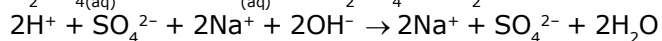
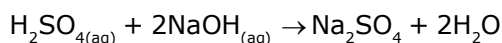


HEAT OF NEUTRALISATION

Enthalpy change during neutralisation of 1 gm equivalent of Acid with 1 gm equivalent of base in dilute solⁿ is called heat of neutralisation.



$$\Delta H^\circ = -13.7 \text{ Kcal}$$

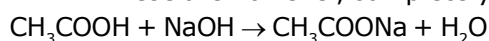


$$\Rightarrow \Delta H = -13.7 \times 2$$

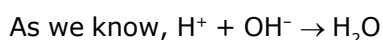
Note :-

In case of weak Acid or weak bases the observed value is little lower because of a part of it is used in dissociating weak Acid or weak base which is not at all completely ionised at dilute solution conditions.

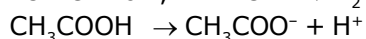
These are however, completely ionised at infinite dilution. e.g.



$$\Delta H = -13.7 + x$$

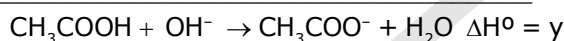


$$\Delta H = -13.7 \text{ kcal} \quad \text{---(1)}$$



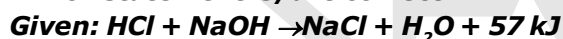
$$\Delta H^\circ = x \quad \text{---(2)}$$

Add eqⁿ (1) + (2)



Ex.12 100 ml 0.5M H_2SO_4 (strong Acid) is neutralised by 200 ml 0.2 M NH_4OH . In a constant pressure calorimeter which results in temperature rise of 1.4°C . If heat capacity of calorimeter constant is $1.5 \text{ kJ}/^\circ\text{C}$.

Which statement is/are correct.



(A) Enthalpy of neutralisation of HCl v/s NH_4OH is -52.5 kJ/mol

(B) Enthalpy of dissociation (ionisation) of NH_4OH is 4.5 kJ/mol

(C) Enthalpy of dissociation of CH_3COOH is 4.6 kJ/mol

(D) ΔH for $2\text{H}_2\text{O(l)} \rightarrow 2\text{H}^+(\text{aq}) + 2\text{OH}^-(\text{aq})$ is 114 kJ

Sol. (A) Total heat evolved due to the neutralization = $C \times \Delta t = 1.5 \times 1.4 = 2.1$

$$\text{M. eq of } \text{H}_2\text{SO}_4 = 100 \times 0.5 = 50$$

$$\text{M. eq of } \text{NH}_4\text{OH} = 20 \times 0.2 = 40$$

Since NH_4OH is limiting hence energy will evolved according to it.

$$\Rightarrow 0.04 \text{ gm eq produces } 2.1 \text{ kJ}$$

$$1 \text{ gm eq produces} = \frac{2.1}{0.04} \times 1 = \frac{210}{4} = 52.5$$

$$\Rightarrow \text{Heat of neutralisation} = -52.5 \text{ kJ}$$

(B) $-57 + x = -52.5$

$$\Rightarrow x = -52.5 + 57 = 4.5$$

$$\Rightarrow \text{Enthalpy of dissociation of } \text{NH}_4\text{OH} = 4.5 \text{ kJ/mol}$$

- (C) $57 - (x + y) = 48.1$
 $\Rightarrow x + y = 8.9$
 $\Rightarrow 4.5 + y = 8.9 \Rightarrow y = 4.4$
 \Rightarrow enthalpy of dissociation of $\text{CH}_3\text{COOH} = 4.4 \text{ kJ/mol}$
- (D) As we know
 $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} \quad \Delta H = -57$
 $\Rightarrow 2\text{H}^+ + 2\text{OH}^- \rightarrow 2\text{H}_2\text{O} \quad \Delta H = -57 \times 2$
 $\Rightarrow 2\text{H}_2\text{O} \rightarrow 2\text{H}^+ + 2\text{OH}^- \quad \Delta H = 114 \text{ kJ}$
 \Rightarrow Option A, B, and D are correct.

BORN HABER CYCLE**Ionisation Energy :-**

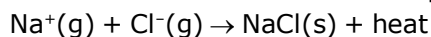
The minimum amount of energy required to remove one electron from the outermost shell of an isolated gaseous atom is called ionisation energy of the element.

Electron affinity:-

Amount of energy released when an extra electron is added to an isolated gaseous atom.

Lattice Energy :

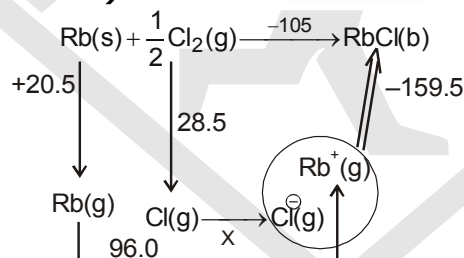
Amount of energy released when 1 mole of gaseous cation and 1 mole gaseous anion combine to each other and form 1 mole of ionic compound is called lattice energy.



↓
Lattice energy

$$\Delta H_{\text{lattice}} \propto \frac{q_1 q_2}{(r^+ + r^-)^2}$$

Ex.13 The born-Haber cycle for formation of rubidium chloride (RbCl) is given bellow (the enthalpies are in kcal mol^{-1})



find the value of X?

Ex.14 Calculate the standard enthalpy change for a reaction $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g})$ given that ΔH_f° for $\text{CO}_2(\text{g})$, $\text{CO}(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ as -393.5 , -110.5 and -241.8 kJ/mol respectively.

- (A) -31.2 kJ (B) -21.2 kJ
 (C) -11.2 kJ (D) $+41.2 \text{ kJ}$

Sol. D

$$\Delta H^\circ = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{Reactants})$$

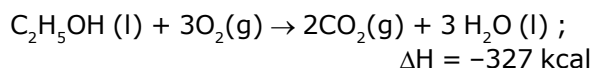
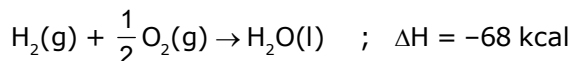
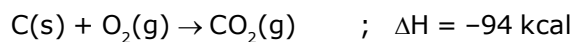
$$= [\Delta H_f^\circ(\text{H}_2\text{O}) + \Delta H_f^\circ(\text{CO})] - [\Delta H_f^\circ(\text{CO}_2) + \Delta H_f^\circ(\text{H}_2)]$$

$$\Delta H^\circ = [-241.8 - 110.5] - [-393.5 + 0]$$

$$= -352.3 + 393.5 = +41.2 \text{ kJ}$$

Class Room Problems

Problems : 1 Find the heat of formation of ethyl alcohol from following data. (Ans. - 65 kcal/mol)



Sol.

Problems : 3 Find ΔH of the following reaction : $\text{OF}_2(\text{g}) + \text{H}_2\text{O(g)} \rightarrow \text{O}_2(\text{g}) + 2\text{HF(g)}$; average bond energies of, O - H, O = O, H - F, O - F, are 44, 111, 118 and 270 kcal/mol respectively.

Sol.

Problem : 4 The heat of formation of ethane is -19.46 kcal. Bond energies of H - H, C - H and C - C bonds are 104.18, 99.0 and 80.0 kcal respectively. Calculate the heat of atomisation of graphite.

Sol.

Problem : 2 Find ΔH_f of HCl(g) if bond energies of H_2 , Cl_2 and HCl are 104, 58, 103 kcal/mol respectively

Sol.

Problem : 5 From Na atoms of an element A, when half atoms transfer one electron to another atom, 405 kJ/mol of energy was found to be consumed. An additional energy of 745 kJ was further required to convert all the A^- ions to A^+ . Calculate the ionisation energy and the electron affinity of atom A in eV.

Sol.

Problems : 7 One mole of naphthalene was burnt in oxygen gas at constant volume to give CO_2 gas and water at $25^\circ C$. The heat evolved was found to be 5138.8 kJ. Calculate heat of reaction at constant pressure.

Sol.

Problems : 6 Enthalpy of neutralisation of acetic acid by NaOH is -50.6 kJ/mol. Calculate ΔH for ionisation of CH_3COOH . Given, the heat of neutralisation of a strong acid with a strong base is -55.9 kJ/mol.

Sol.

Problems : 8 Calculate the heat of combustion of benzene(l) at standard conditions. Given that the standard enthalpies of formation of $C_6H_6(l)$, $H_2O(l)$ and $CO_2(g)$ are 49, -286.2 and -393.5 Kcal/mole respectively.

Sol.

Problems : 9 0.6 gm of carbon was converted into CO_2 producing 4800 calorie of heat. When 0.6 gm of C converted to CO 1450 calories of heat was produced. What will be heat produced when 1.4 gm of CO is converted to CO_2 .

Sol.

Sol.

Problems : 10 Calculate standard heat of formation of CS_2 . Given that standard heat of combustion of C, S and CS_2 are -393.3, -293.72 and -1108.76 KJ/mole.

Sol.

Problems : 12 The enthalpy change involved in the oxidation of glucose is -2880 KJ/mole. Twenty five percent of this energy is available for muscular work. If 100 KJ of muscular work is needed to walk one kilometer, what is the maximum distance that person will be able to walk after eating 120 gm of glucose.

Sol.

Problems : 11 Calculate the mass of mercury which can be liberated from HgO at 25°C by the treatment of excess of HgO with 41.85 KJ of heat at (a) constant pressure and (b) constant volume conditions : Given $\Delta H_f^\circ [\text{HgO(s)}] = -90.8 \text{ KJ/mole}$, $M(\text{Hg}) = 200.6 \text{ gm/mole}$.

Problems : 13 15.5 gm carbon is treated with 25 litre of air at 25°C and 5.5 atm (air contain 19% by volume O_2). Determine the heat evolved under constant pressure if after reaction carbon and oxygen are completely consumed. $\Delta H_f^\circ [\text{CO}_2(\text{g})] = -94.05 \text{ KJ/mole}$

$\Delta H_f^\circ [\text{CO(g)}] = -26.71 \text{ KJ/mole}$.

Sol.

Problems : 14 Estimate ΔH for $2C_4H_{10}(g) \rightarrow C_8H_{18}(g) + H_2(g)$. Given bond energy of C—C, C—H are 347.3 and 414.2 KJ/mole. The heat of formation of H atom is 217.55 KJ/mole.

Sol.

Problems : 16 The heat of combustion of acetylene is 312 Kcal. If the heat of formation of CO_2 is 94.38 Kcal and that of water is 68.38 Kcal. Calculate $C \equiv C$ bond energy assuming that the bond energy of C—H is 93.6 Kcal. heat of atomisation of carbon and hydrogen are 150 and 51.5 Kcal respectively.

Sol.

Problems : 15 Calculate ΔH for the following homogeneous gaseous reaction $CH_3COCH_3 + 2O_2 \rightarrow CH_3COOH + CO_2 + H_2O$. Given Bond energy : C—H : 99 Kcal C—C : 83 Kcal, C = O : 173 Kcal O=O : 118 Kcal ; C—O : 84 ; O—H : 110 Kcal.

Sol.

Problems : 17 Calculate the resonance energy of C_6H_6 from the following data (a) H_f° for $C_6H_6 = -358.5$ KJ/mole (b) Heat of atomisation of C : 716.8 KJ/mole (c) Bond energies of C—H, C—C, C=C, and H—H are 490, 340, 620 and 436.9 KJ/mole respectively.

Sol.

Problems : 18 Calculate the lattice energy of $\text{AlH}_3(\text{s})$ from the following data : $\Delta H_{\text{formation}}^{\circ} [\text{AlH}_3(\text{s})] = -52$ Kcal/mol, $\Delta H_{\text{sublimation}}^{\circ} [\text{Al}(\text{s})] = 15$ Kcal/mol, $\Delta H_{\text{fusion}}^{\circ} [\text{Iodine}(\text{s})] = 10$ Kcal/mol, $\Delta H_{\text{vapourization}}^{\circ} [\text{Iodine}(\text{l})] = 6$ Kcal/mol, $\Delta H_{\text{EA}}^{\circ} [\text{Iodine}(\text{g})] = -28.67$ Kcal/mol, B.E. of (I-I) = 5 Kcal/mol. The sum of first two ionization energies and 3 times the third is 74 Kcal/mol. The sum of the first and third ionization energies along with twice the second ionization energy is 54 Kcal/mol, while three times the first ionization energy added to five times the third ionization energy subtracted by the second ionization energy given 98 Kcal/mol.

Sol.

Problems : 19 A 150 ml of 0.5N HCl is neutralised with an excess of NH_4OH in a vessel with a rise of temperature 2.36°C . If the heat capacity of vessel and its content after the reaction is 315 cal/deg. Calculate heat of neutralisation in cal./mole.

Sol.

Problems : 20 The molar heat capacities for $\text{H}_2\text{O}(\text{s})$ and $\text{H}_2\text{O}(\text{l})$ are $37.7 \text{ J mole}^{-1} \text{ K}^{-1}$ and $75.3 \text{ J mole}^{-1} \text{ K}^{-1}$ respectively. The enthalpy of fusion of ice at -10°C is 5.627 KJ/mole . Calculate the enthalpy of fusion of ice at 0°C . Assuming that molar heat capacities are independent of temperature in this range.

Sol.

Problems : 21 3.5 gm of a fuel (mo. wt. = 28) was burnt in a calorimeter and raised the temperature of 1 gm water from 25°C to 67.3°C . If all the heat generated was used in heating water, calculate heat of combustion of fuel.

Sol.

EXERCISE – I

OBJECTIVE PROBLEMS (JEE MAIN)

1. For which of the following change $\Delta H \neq \Delta E$?

- (A) $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g})$
 (B) $\text{HCl}(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
 (C) $\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$
 (D) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$

Sol.

2. $\Delta_r H$ of which of the following reactions is zero ?

- (A) $\text{H}_2(\text{g}) \rightarrow 2\text{H}^+(\text{g}) + 2\text{e}^-$
 (B) $2\text{H}(\text{g}) + \text{aq} \rightarrow 2\text{H}^+(\text{aq}) + 2\text{e}^-$
 (C) $2\text{H}(\text{g}) \rightarrow 2\text{H}^+(\text{g}) + 2\text{e}^-$
 (D) $\text{H}_2(\text{g}) + \text{aq} \rightarrow 2\text{H}^+(\text{aq}) + 2\text{e}^-$

Sol.

3. How much heat will be required at constant pressure to form 1.28 kg of CaC_2 from $\text{CaO}(\text{s})$ & $\text{C}(\text{s})$?

Given : $\Delta_f H^\circ(\text{CaO}, \text{s}) = -152 \text{ kcal/mol}$

$\Delta_f H^\circ(\text{CaC}_2, \text{s}) = -14 \text{ kcal/mol}$

$\Delta_f H^\circ(\text{CO}, \text{g}) = -26 \text{ kcal/mol}$

- (A) +112 kcal (B) 224 kcal
 (C) 3840 kcal (D) 2240 kcal

Sol.

4. 50.0 mL of 0.10 M HCl is mixed with 50.0 mL of 0.10 M NaOH. The solution temperature rises by 3.0°C . Calculate the enthalpy of neutralization per mole of HCl. [take proper assumptions]

- (A) $-2.5 \times 10^2 \text{ kJ}$ (B) $-1.3 \times 10^2 \text{ kJ}$
 (C) $-8.4 \times 10^1 \text{ kJ}$ (D) $-6.3 \times 10^1 \text{ kJ}$

Sol.

5. The enthalpy of neutralisation of a weak acid in 1 M solution with a strong base is $-56.1 \text{ kJ mol}^{-1}$. If the enthalpy of ionization of the acid is 1.5 kJ mol^{-1} and enthalpy of neutralization of the strong acid with a

strong base is $-57.3 \text{ kJ equiv}^{-1}$, what is % ionization of the weak acid in molar solution (assume the acid to be monobasic) ?

- (A) 10 (B) 15 (C) 20 (D) 80

Sol.

6. For the allotropic change represented by the equation $\text{C}(\text{graphite}) \rightarrow \text{C}(\text{diamond})$, $\Delta H = 1.9 \text{ kJ}$. If 6 g of diamond and 6 g of graphite are separately burnt to yield CO_2 , the heat liberated in first case is

- (A) less than in the second case by 1.9 kJ
 (B) more than in the second case by 11.4 kJ
 (C) more than in the second case by 0.95 kJ
 (D) less than in the second case by 11.4 kJ

Sol.

7. If x_1 , x_2 and x_3 are enthalpies of $\text{H}-\text{H}$, $\text{O}=\text{O}$ and $\text{O}-\text{H}$ bonds respectively, and x_4 is the enthalpy of vaporisation of water, estimate the standard enthalpy of combustion of hydrogen

- (A) $x_1 + \frac{x_2}{2} - 2x_3 + x_4$ (B) $x_1 + \frac{x_2}{2} - 2x_3 - x_4$
 (C) $x_1 + \frac{x_2}{2} - x_3 + x_4$ (D) $2x_3 - x_1 - \frac{x_2}{2} - x_4$

Sol.

8. $\text{NH}_3(\text{g}) + 3\text{Cl}_2(\text{g}) \rightleftharpoons \text{NCl}_3(\text{g}) + 3\text{HCl}(\text{g}) ; -\Delta H_1$
 $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g}) ; \Delta H_2$
 $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{HCl}(\text{g}) ; \Delta H_3$
 The heat of formation of $\text{NCl}_3(\text{g})$ in the terms of ΔH_1 , ΔH_2 and ΔH_3 is

- (A) $\Delta H_f = -\Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$
 (B) $\Delta H_f = \Delta H_1 + \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$
 (C) $\Delta H_f = \Delta H_1 - \frac{\Delta H_2}{2} - \frac{3}{2}\Delta H_3$ (D) None

Sol.

9. The enthalpy of neutralisation of HCl and NaOH is -57 kJ mol^{-1} . The heat evolved at constant pressure (in kJ) when 0.5 mole of H_2SO_4 react with 0.75 mole of NaOH is equal to

- (A) $57 \times \frac{3}{4}$ (B) 57×0.5 (C) 57 (D) 57×0.25

Sol.

10. Reaction involving gold have been of particular interest to a chemist. Consider the following reactions.
 $\text{Au}(\text{OH})_3 + 4\text{HCl} \rightarrow \text{HAuCl}_4 + 3\text{H}_2\text{O}, \Delta H = -28 \text{ kcal}$
 $\text{Au}(\text{OH})_3 + 4\text{HBr} \rightarrow \text{HAuBr}_4 + 3\text{H}_2\text{O}, \Delta H = -36.8 \text{ kcal}$
 In an experiment there was an absorption of 0.44 kcal when one mole of HAuBr_4 was mixed with 4 moles of HCl. What is the percentage conversion of HAuBr_4 into HAuCl_4 ?

- (A) 0.5 % (B) 0.6 % (C) 5 % (D) 50%

Sol.

11. (i) Cis - 2 - butene \rightarrow trans - 2 - butene, ΔH_1
 (ii) Cis - 2 - butene \rightarrow 1 - butene, ΔH_2
 (iii) Trans - 2 - butene is more stable than cis - 2 - butene.
 (iv) Enthalpy of combustion of 1 - butene, $\Delta H = -649.8 \text{ kcal/mol}$
 (v) $9\Delta H_1 + 5\Delta H_2 = 0$
 (vi) Enthalpy of combustion of trans 2 - butene, $\Delta H = -647.0 \text{ kcal/mol}$
 The value of ΔH_1 & ΔH_2 in Kcal/mole are
 (A) -1.0, 1.8 (B) 1.8, -1.0 (C) -5, 9 (D) -2, 3, 6

Sol.

12. The reaction $\text{CH}_4(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow \text{CH}_3\text{Cl}(\text{g}) + \text{HCl}(\text{g})$ has $\Delta H = -25 \text{ kCal}$.

Bond	Bond Energy kCal
$\epsilon_{\text{C}} - \text{Cl}$	84
$\epsilon_{\text{H}} - \text{Cl}$	103
$\epsilon_{\text{C}} - \text{H}$	x
$\epsilon_{\text{Cl}} - \text{Cl}$	y
$x : y = 9 : 5$	

From the given data, what is the bond energy of Cl - Cl bond

- (A) 70 kCal (B) 80 kCal (C) 67.75 kCal (D) 57.75 kCal

Sol.

13. From the following data at 25°C

Reaction	$\Delta_r H^\circ$ kJ/mol
$\frac{1}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{OH}(\text{g})$	42
$\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g})$	-242
$\text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{g})$	436
$\text{O}_2(\text{g}) \rightarrow 2\text{O}(\text{g})$	495

Which of the following statement(s) is/are correct :

Statement(a) : $\Delta_r H^\circ$ for the reaction $\text{H}_2\text{O}(\text{g}) \rightarrow 2\text{H}(\text{g}) + \text{O}(\text{g})$ is 925 kJ/mol

Statement(b) : $\Delta_r H^\circ$ for the reaction $\text{OH}(\text{g}) \rightarrow \text{H}(\text{g}) + \text{O}(\text{g})$ is 502 kJ/mol

Statement(c) : Enthalpy of formation of $\text{H}(\text{g})$ is -218 kJ/mol

Statement(d) : Enthalpy of formation of $\text{OH}(\text{g})$ is 42 kJ/mol

- (A) Statement c (B) Statement a, b, d
(C) Statement b, c (D) Statement a, d

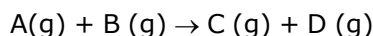
Sol.

14. The standard molar enthalpies for formation of cyclohexane (l) & benzene (l) at 25°C are -156 & +49 kJ/mol respectively. The standard enthalpy of hydrogenation of cyclohexene (l) at 25° is -119 kJ mol⁻¹. Use these data to estimate the magnitude of the resonance energy of benzene.

- (A) 252 kJ mol⁻¹ (B) 240 kJ mol⁻¹
(C) 152 kJ mol⁻¹ (D) None of these

Sol.

15. For hypothetical reaction -



Which of the following statements is correct -

- (A) $\Delta H = \Delta E$ (B) $\Delta H > \Delta E$
(C) $\Delta H < \Delta E$ (D) unpredictable

Sol.

16. ΔH for $\text{CaCO}_{3(\text{s})} \rightarrow \text{CaO}_{(\text{s})} + \text{CO}_{2(\text{g})}$ is 176 kJ mol⁻¹ at 1240 K. The ΔU for the change is equal to :

- (A) 160 kJ (B) 165.6 kJ
(C) 186.3 kJ (D) 180.0 kJ

Sol.

17. Select the correct order in the following :

- (A) 1 erg > 1 joule > 1 cal
(B) 1 cal > 1 joule > 1 erg
(C) 1 erg > 1 cal > 1 joule
(D) 1 joule > 1 cal > 1 erg

Sol.

18. Difference between ΔH and ΔE for the combustion of liquid benzene at 27°C is -

- (A) 7.48 kJ (B) 3.74 kJ
(C) 14.86 kJ (D) 5.73 kJ

Sol.

19. In the combustion of 4g. of CH_4 , 2.5 K cal of heat is liberated. The heat of combustion of CH_4 is -
 (A) 20 K. cal (B) 10 K. cal
 (C) 2.5 K. cal (D) 5 K. cal

Sol.

20. Ammonium nitrate can decompose with explosion by the following reaction.
 $\text{NH}_4\text{NO}_3 (\text{s}) \rightarrow \text{N}_2\text{O} (\text{g}) + 2\text{H}_2\text{O}$;
 $\Delta H = -37.0 \text{ KJ/mol}$
 Calculate the heat produced when 2.50g of NH_4NO_3 decomposes -
 (A) 1.06 KJ (B) 0.96KJ
 (C) 1.16 KJ (D) 1.26 KJ

Sol.

21. From the following data, the heat of formation of $\text{Ca}(\text{OH})_2(\text{s})$ at 18°C iskcal:
 $\text{CaO}(\text{s}) + \text{H}_2\text{O}(\text{l}) \longrightarrow \text{Ca}(\text{OH})_2(\text{s})$;
 $\Delta H_{18^\circ\text{C}} = -15.26 \text{ kcal} \quad \dots (i)$
 $\text{H}_2\text{O}(\text{l}) \longrightarrow \text{H}_{2(\text{g})} + \frac{1}{2} \text{O}_{2(\text{g})}$;
 $\Delta H_{18^\circ\text{C}} = 68.37 \text{ kcal} \dots(ii)$
 $\text{Ca}_{(\text{s})} + \frac{1}{2} \text{O}_{2(\text{g})} \longrightarrow \text{CaO}_{(\text{s})}$;
 $\Delta H_{18^\circ\text{C}} = -151.80 \text{ kcal} \dots (iii)$
 (A) -98.69 (B) -235.43
 (C) 194.91 (D) 98.69

Sol.

22. For the process, melting of ice at 260 K the ΔH is -
 (A) Negative
 (B) Positive
 (C) Zero
 (D) Cannot be predicted

Sol.

23. Enthalpy of formation of compound is -
 (A) always positive
 (B) always negative
 (C) can be either negative or zero
 (D) can be positive or negative

Sol.

24. The enthalpy of combustion of a substance -
 (A) is always positive
 (B) is always negative
 (C) can be either zero or greater than zero
 (D) is unpredictable till calculations are done.

Sol.

25. $\text{HA} + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{A}^- + q_1 \text{ kJ}$
 $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} + q_2 \text{ kJ}$
The enthalpy of dissociation of HA is
(A) $(q_1 + q_2)$ (B) $(q_1 - q_2)$
(C) $(q_2 - q_1)$ (D) $-(q_1 + q_2)$

Sol.

26. The value of $\Delta H_{\text{sol.}}$ of $\text{BaCl}_2(\text{s})$ and $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}(\text{s})$ are $-a \text{ kJ}$ and $b \text{ kJ}$ respectively. The value of $\Delta H_{\text{Hydration}}$ of $\text{BaCl}_2(\text{s})$ is -
(A) $b - a$ (B) $a + b$
(C) $-a - b$ (D) $a - b$

Sol.

27. A solution of 500 ml of 0.2 M KOH and 500 ml of 0.2 M HCl is mixed and stirred; the rise in temperature is T_1 . The experiment is repeated using 250 ml of each solution, the temperature raised is T_2 . Which of the following is true -
(A) $T_1 = T_2$ (B) $T_1 = 2T_2$
(C) $T_1 = 4T_2$ (D) $T_2 = 9T_1$

Sol.

28. The net heat change in a chemical reaction is same whether it is brought about in two or more different ways in one or several steps. It is known as -
(A) Hess's law
(B) Law of conservation of energy
(C) Henry's law
(D) Joule's principle

Sol.

29. According to Hess's Law the thermal effect of a reaction depends on -
(A) initial concentration of reactants
(B) final condition of the reacting substance
(C) intermediate states of a reaction
(D) initial and final conditions of the reacting substances

Sol.

30. How many kcal of heat is evolved by the complete neutralisation of one mole sulphuric acid with NaOH -
(A) 13.7 kcal
(B) 27.4 kcal
(C) 6.85 kcal
(D) None of the above

Sol.

31. Given that $\Delta H_{\text{comb.}}$ of cyclopropane is $-4000 \text{ kJ mol}^{-1}$. The amount of cyclopropane that needs to be burnt in oxygen for producing $2 \times 10^5 \text{ kJ}$ of heat is -

(A) 20 kg (B) 2.1 kg
(C) 21 g (D) 210 mg

Sol.

32. The latent heats of fusion in J g^{-1} of five substances a (mol. mass = 18) ; b (mol. mass = 20) ; c (mol. mass = 30), d (mol. mass = 60) and e (mol. mass = 30) are respectively 80, 45, 90, 45, 45. Which of the following pair has same value of ΔH_{fusion} -

(A) a,c (B) b,e
(C) d,e (D) c, d

Sol.

33. Heats of combustion of CH_4 , C_2H_6 , C_3H_8 , C_8H_{18} in K. cal/mole $^{-1}$ as -210.8 , -368.4 , -526.3 , -1302.7 respectively. Decide which is a better rocket fuel -

(A) C_8H_{18} (B) CH_4
(C) C_3H_8 (D) C_2H_6

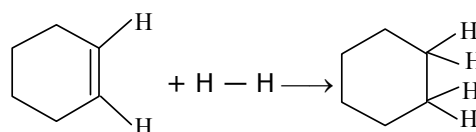
Sol.

34. The enthalpy of neutralization of NH_4OH and CH_3COOH is -10.5 kcal/mole and enthalpy of neutralization of strong base and CH_3COOH is -12.5 kcal/mole . Calculate the enthalpy of dissociation of NH_4OH -

(A) 3.0 (B) 4.0
(C) 2.0 (D) 10.0

Sol.

35. For the reaction,



bond energies are given as under -

- (i) $\text{C}-\text{C}$, 346 kJ/mol
(ii) $\text{C}-\text{H}$, 413 kJ/mol
(iii) $\text{H}-\text{H}$, 437 kJ/mol and
(iv) $\text{C}=\text{C}$, 611 kJ/mol

What will be the value of ΔH at 25°C for the above reaction ?

(A) -289 kJ mol^{-1} (B) -124 kJ mol^{-1}
(C) $+124 \text{ kJ mol}^{-1}$ (D) $+289 \text{ kJ mol}^{-1}$

Sol.

36. The bond enthalpies of H_2 , X_2 and HX are in the ratio of $2 : 1 : 2$. if the enthalpy for formation of HX is -50 kJ mol^{-1} , the bond enthalpy of H_2 is -

(A) 200 kJ mol^{-1} (B) 400 kJ mol^{-1}
(C) 100 kJ mol^{-1} (D) 300 kJ mol^{-1}

Sol.

37. The heat of combustion of ethylene $C_2H_4(g)$ is -1420 kJ/mole . The volume of C_2H_4 at NTP that would evolve 355 kJ on combustion is -
 (A) 2.8 lit (B) 8.4 lit (C) 5.6 lit (D) 11.2 lit

Sol.

38. The heat produced by complete neutralisation of 100 ml of HNO_3 with 300 ml of decimolar KOH solution is 1.713 kJ . The molarity of HNO_3 solution will be -

- (A) 0.1 (B) 1
 (C) 0.3 (D) 0.5

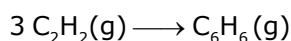
Sol.

39. When ethyne is passed through a red hot tube, then formation of benzene takes place -

$$\Delta H_f^\circ(C_2H_2)(g) = 230 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ(C_6H_6)(g) = 85 \text{ kJ mol}^{-1}$$

Calculate the standard heat of trimerisation of ethyne to benzene.



- (A) 205 kJ mol^{-1} (B) 605 kJ mol^{-1}
 (C) -605 kJ mol^{-1} (D) -205 kJ mol^{-1}

Sol.

40. The value of ΔH° for the reaction $Cu^+(g) + I^-(g) \rightarrow CuI(g)$ is -446 kJ mol^{-1} . If

the ionization energy of $Cu(g)$ is 745 kJ mol^{-1} and the electron affinity of $I(g)$ is -295 kJ mol^{-1} , then the value of ΔH° for the formation of one mole of $CuI(g)$ from $Cu(g)$ and $I(g)$ is -

- (A) -446 kJ (B) 450 kJ
 (C) 594 kJ (D) 4 kJ

Sol.

41. The lattice enthalpy and hydration enthalpy of four compounds are given below -

Compound	Lattice enthalpy (kJ/mol)	Hydration enthalpy (kJ/mol)
P	+780	-920
Q	+1012	-812
R	+828	-878
S	+632	-600

The pair of compounds which is soluble in water is -

- (A) P and Q (B) Q and R
 (C) R and S (D) P and R

Sol.

42. A mixture of hydrogen gas and the theoretical amount of air at 25°C and a total pressure of 1 atm , is exploded in a **closed rigid vessel**. If the process occurs under **adiabatic condition** then using the given data answer the questions that follow :

Given (i) $C_p = 8.3 \text{ cal deg}^{-1} \text{ mol}^{-1}$;

(ii) $C_p = 11.3 \text{ cal deg}^{-1} \text{ mol}^{-1}$; $\Delta H_f[H_2O(g)] = -57.8 \text{ K cal}$
 [Take air as 80% N_2 , 20% O_2 by volume]

(i) The value of C_p of N_2 & H_2O will be (in $\text{cal. deg}^{-1} \text{ mol}^{-1}$)
 (A) 8.3, 8.3 (B) 8.3, 11.3 (C) 11.3, 11.3 (D) 11.3, 8.3

Sol.

(ii) What will be the maximum temperature attained if the process occurs in adiabatic container.

(A) $\cong 2940$ K (B) $\cong 2665$ K (C) $\cong 1900$ K (D) $\cong 298$ K

Sol.

(iii) What will be the final pressure in atm.

(A) $\cong 8.5$ (B) $\cong 7.6$ (C) $\cong 5.46$ (D) $\cong 0.85$

Sol.

(iv) If at initial temperature T_1 , E_1 is initial internal energy & at higher final temperature T_2 , E_2 is the final internal energy, then which option is true

(A) $E_1 > E_2$ (B) $E_2 > E_1$ (C) $E_1 = E_2$
(D) can't be compared from the given data

Sol.

Sol.

44. Heat evolved in the reaction $H_2 + Cl_2 \rightarrow 2HCl$ is 182 KJ. Bond energies H - H = 430 KJ/ mole, Cl - Cl = 242 KJ/ mole. The H - Cl bond energy is-

(A) 763 kJ mole⁻¹ (B) 427 kJ mole⁻¹
(C) 336 kJ mole⁻¹ (D) 154 kJ mole⁻¹

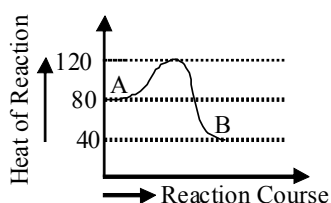
Sol.

45. Heat of neutralisation of HF is -

(A) 57.32 kJ (B) > 57.32 kJ
(C) < 57.32 (D) None

Sol.

43. According to the diagram given below, the value of ΔH for conversion of A to B is -



(A) - 40 (B) + 40
(C) -120 (D) + 120

46. The heat of neutralisation is constant when dilute solution of -

(A) strong acid and strong base react
(B) strong acid and weak base react
(C) strong base and weak acid react
(D) in all the cases

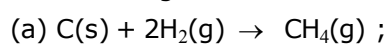
Sol.

- 47.** How much heat is liberated when 100 mL of 0.1 M NaOH are completely neutralised by 100 mL of 0.1 M HCl -

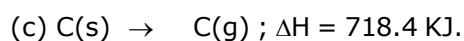
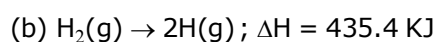
(A) - 57 kJ (B) - 0.57 kJ
(C) - 5.7 kJ (D) - 0.05 kJ

Sol.

- 48.** Calculate the bond energy of C-H bond from the following data :



$$\Delta H = -74.8 \text{ KJ}$$



(A) 316.0 KJ/mol (B) 416 KJ/mol
(C) 516 KJ/mol (D) 616.0 KJ/mol

Sol.

- 49.** The enthalpy of the reaction $\text{H}_2\text{O}_2(\ell) \rightarrow \text{H}_2\text{O}(\ell) + 1/2 \text{O}_2(\text{g})$ is - 23.5 kcal mol⁻¹ and the enthalpy of formation of $\text{H}_2\text{O}(\ell)$ is - 68.3 kcal mol⁻¹. The enthalpy of formation of $\text{H}_2\text{O}_2(\ell)$ is -
(A) - 44.8 kcal mol⁻¹ (B) 44.8 kcal mol⁻¹
(C) - 91.8 kcal mol⁻¹ (D) 91.8 kcal mol⁻¹

Sol.

- 50.** Enthalpy change of the reaction $2\text{H(g)} \rightarrow \text{H}_2(\text{g})$ is - 104 kcal
The H - H bond dissociation energy is-
(A) 104 kcal (B) -104 kcal
(C) - 52 kcal (D) + 52 kcal

Sol.

EXERCISE – II**OBJECTIVE PROBLEMS (JEE ADVANCED)**

1. Which of the following pairs are correctly matched ?

- (A) Arrhenius equation : Variation of enthalpy of a reaction with temperature
 (B) Kirchoff equation : Variation of rate constant with temperature
 (C) Second law of : Entropy of an isolated system tends to increase and reach a maximum value thermodynamics
 (D) Hess's law of constant : Enthalpy change in a reaction is always constant and independent of the heat summation manner in which the reaction occurs

Sol.

2. Which of the following statements is (are) correct

- (A) The heat of neutralization of a strong acid with a strong base is always the same
 (B) The enthalpy of combustion is always negative
 (C) A spontaneous change involves a lowering of free energy
 (D) The enthalpy of an element in the standard state is assumed to be unity at 298 K

Sol.

3. Which is (are) correct for ideal gas ?

- (A) $\left(\frac{\delta U}{\delta T}\right)_P = 0$ (B) $\left(\frac{\delta U}{\delta T}\right)_H = 0$
 (C) $\left(\frac{\delta E}{\delta V}\right)_T = 0$ (D) $\left(\frac{\delta U}{\delta P}\right)_T = 0$

Sol.

4. Which of the following are applicable for a thermochemical equation ? It tells :

- (A) About the physical state of reactants and products
 (B) About the allotropic form (if any) of the reactants
 (C) Whether the reaction is exothermic or endothermic
 (D) Whether a particular reaction is spontaneous or not

Sol.

5. The heat of reaction depends upon :

- (A) The manner by which the reaction is carried out
 (B) Temperature at which the reaction is carried out
 (C) Physical state of reactant and products
 (D) Whether the reaction is carried out at constant pressure or at constant volume

Sol.

6. The enthalpy of formation of $\text{UF}_6(\text{g})$ is 22 kcal mol^{-1} and that of $\text{U}(\text{g})$ is $128 \text{ kcal mol}^{-1}$. The bond energy of the $\text{F} - \text{F}$ bond is 37 kcal mol^{-1} . The bond dissociation energy of $\text{UF}_6(\text{g})$ is (are) :

- (A) $124.5 \text{ kcal mol}^{-1}$ (B) $131.1 \text{ kcal mol}^{-1}$
 (C) 521 kJ mol^{-1} (D) 623 kJ mol^{-1}

Sol.

7. The standard heat of formation of a compound is the :

- (A) Change in enthalpy for the production of 1 mole of the compound at STP
- (B) Change in enthalpy for the formation of 1 mole of the compound from its elements
- (C) Change in enthalpy for the formation of 1 mole of the compound from its elements at 298 K and 1 atm pressure
- (D) Change in enthalpy for the formation of 1 mole of the compound from its elements at 25°C and 760 mm of Hg pressure

Sol.

8. The heat of neutralization of a strong acid by a strong base is a constant because :

- (A) The strong acid and strong base react completely
- (B) The strong acid and strong base dissociate completely and only H^+ and OH^- ions react in every case
- (C) The salt formed do not hydrolyse
- (D) There is no side reaction during neutralization

Sol.

9. Which of the following statements is (are) true ?

- (A) The evaporation of water is an endothermic change
- (B) The conversion of white phosphorus to red phosphorus is an exothermic reaction
- (C) The heat of neutralisation of a strong acid with a strong base is always the same
- (D) ΔH is negative for endothermic reactions

Sol.

10. The standard heat of formation of U_3O_8 is $-853.5 \text{ kcal mol}^{-1}$ and standard heat of the reaction, $3UO_2 + O_2 \rightarrow U_3O_8$ is -76.01 kcal . The standard heat of formation of UO_2 is (are) :

- (A) $-1083 \text{ kJ mol}^{-1}$
- (B) $-1102 \text{ kJ mol}^{-1}$
- (C) $-259 \text{ kcal mol}^{-1}$
- (D) $-302 \text{ kcal mol}^{-1}$

Sol.

11. For which of the following substances is the heat of formation in the standard state zero ?

- (A) Aluminium
- (B) C_{diamond}
- (C) Zinc
- (D) C_{graphite}

Sol.

12. Which of the following statements is (are) true ?

- (A) ΔH is $-ve$ for exothermic reactions
- (B) ΔH is $+ve$ for endothermic reactions
- (C) The heat of neutralization of strong acid and strong bases is constant
- (D) The enthalpy of fusion is $+ve$

Sol.

13. The heat of combustion of ethanol was determined in a bomb calorimeter and was found to be $-670.48 \text{ kcal mol}^{-1}$ at 25°C. What will be ΔU for the same reaction at 298 K ?

- (A) -2802.6 kJ
- (B) -669.28 cal
- (C) -670.48 kcal
- (D) $-280.26 \times 10^4 \text{ J}$

Sol.

14. Match the column

Column I

- (A) $\text{N}_{2(g)} + \text{O}_{2(g)} \rightarrow 2\text{NO}_{(g)}$
 (B) $2\text{KI}_{(g)} + \text{HgI}_{2(aq)} \rightarrow \text{K}_2[\text{HgI}_4]_{(aq.)}$
 (C) $\text{PCl}_{3(g)} + \text{Cl}_{2(g)} \rightarrow \text{PCl}_{5(g)}$
 (D) $\text{NH}_{3(g)} + \text{HCl}_{(g)} \rightarrow \text{NH}_4\text{Cl}_{(s)}$

Column II

- (P) $\Delta S > 0$
 (Q) $\Delta S < 0$
 (R) $\Delta H > 0$
 (S) $\Delta H < 0$

Sol.

15. Match the column

Column I

- (A) Kirchoff's equation
 (B) ΔH
 (C) $\frac{q_{\text{rev}}}{T}$

Column II

- (P) $\frac{d}{dt}(\Delta H) = \Delta C_p$
 (Q) $\Delta U + \Delta n RT$
 (R) ΔS
 (S) $\frac{\Delta H_2 - \Delta H_1}{\Delta T} = \Delta C_p$

Sol.**COMPREHENSION - I**

Heat of reaction is the change in enthalpy or internal energy as represented by a balanced thermochemical equation. The amount of energy released during a chemical change depends upon the state of reactants and products, the conditions of pressure and volume at which reaction is carried out, and temperature. The variation of heat of reaction (ΔH or ΔE) with temperature is given as $\Delta H_2 - \Delta H_1 = \Delta C_p [T_2 - T_1]$ or $\Delta E_2 - \Delta E_1 = \Delta C_v (T_2 - T_1)$. Standard heat enthalpy of elements in their most stable state is assumed to be zero whereas standard heat enthalpy of compound is referred as heat of formation of that compound at 1 atm pressure and 25°C. Oxidation of N_2 to N_2O , NO,

NO_2 shows absorption of energy whereas heat of combustion of N_2 is exothermic like other heat of combustion.

16. Standard heat enthalpy has been assumed to be zero for :

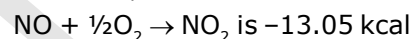
- (A) Graphite (B) Diamond (C) Charcoal (D) Lamp black

Sol.

17. Which statements regarding the formation of NO and NO_2 respectively from N_2 and O_2 are correct :

- (A) Heat of formation of NO is exothermic
 (B) Heat of formation of NO_2 is exothermic
 (C) The oxidation of N_2 to NO and NO_2 is favoured at high temperature.

(D) If heat of formation of NO and NO_2 are 21.55 and 8.50 kcal, heat of reaction for



- (A) 1, 2 (B) 3, 4 (C) 1, 2, 4 (D) 1, 2, 3

Sol.

18. Heat of combustion of carbon in diamond and amorphous form are -94.3 and -97.6 kcal/mole. The heat required to convert 6 g carbon from diamond to amorphous form is :

- (A) -1.65 kcal (B) +1.65 kcal
 (C) -3.3 kcal (D) +3.3 kcal

Sol.

19. Heat of vaporisation of H_2O is 627.78 cal/g. If heat of formation of $\text{H}_2\text{O}_{(l)}$ is -68.3 kcal, heat of formation of $\text{H}_2\text{O}_{(g)}$ is :

- (A) -57.0 kcal (B) 559.5 kcal
(C) 676.73 kcal (D) Can not be calculated

Sol.

20. The specific heat of I_2 in vapour and solid state are 0.031 and 0.055 cal/g-°C respectively. If heat of sublimation of iodine is 6.096 kcal mol⁻¹ at 200°C, the heat of sublimation of I_2 at 250°C is :

- (A) 5.8 kcal mol⁻¹ (B) 2.28 kcal mol⁻¹
(C) 4.8 kcal mol⁻¹ (D) 3.8 kcal mol⁻¹

Sol.

Sol.

22. Which of the following statements are correct :

- (1) $\Delta H = \Delta U + \Delta nRT$
(2) Heat changes measured by bomb calorimeter give change in heat enthalpy during the reaction.
(3) $\Delta H = \Delta U$ for the reaction :
 $\text{C}_{(s)} + \text{O}_{2(g)} \rightarrow \text{CO}_{2(g)}$
(4) Heat of formation for C_6H_6 can be directly measured
(A) 2, 3 (B) 1, 4 (C) 1, 2, 3 (D) 1, 3

Sol.

23. 200 mL of 0.1 M NaOH is mixed with 100 mL of 0.1 M H_2SO_4 in I experiment. In II experiment 100 mL of 0.1 M NaOH is mixed with 50 mL of 0.1 M H_2SO_4 .

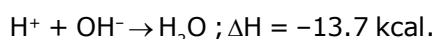
Select the correct statements :

- (1) Heat liberated in each of the two reactions is 274 cal.
(2) Heat liberated in I is 274 cal and in II is 137 cal
(3) Temperature rise in I reaction is more than the temperature rise in II.
(4) Temperature rise in I reaction is equal to the temperature rise in II.
(A) 1, 3 (B) 2, 4 (C) 2, 3 (D) 1, 4

Sol.

COMPREHENSION - II

Heat of neutralisation is amount of heat evolved or absorbed when 1 g-equivalent of an acid reacts with 1 g-equivalent of a base in dilute solution. If weak acid or weak base are neutralised, the heat released during neutralisation is some what lesser than -13.7 kcal or -57.27 kJ. Heat of neutralisation is also referred as heat of formation of water from H^+ and OH^- ions i.e.,



21. Heat of neutralisation of HF and acetic acid respectively are (in kcal) :

- (A) > -13.7, < -13.7 (B) > -13.7
(C) < -13.7 (D) < -13.7, > -13.7

COMPREHENSION - III

Hess's law of heat of summation is based on law of conservation of energy. It has found significance in deriving heats of many reactions which either do not take place or if take place, than other side reactions also accompany it. For example heat of reaction for $C + \frac{1}{2} O_2 \rightarrow CO$ can not be studied directly as it occurs with simultaneous reaction of oxidation of CO to CO_2 . Bond energy is referred as heat enthalpy when a bond is broken to produce isolated gaseous atoms. In case of breaking up of bonds between unlike atoms e.g., C - H bond in CH_4 , bond energy is referred as average bond energy as four C - H bonds are broken up.

24. Which of the following statements are correct :

- (1) The dissociation of bond is always endothermic.
- (2) The formation of a bond is always exothermic.
- (3) Heat of formation of an atom = $\frac{1}{2} \times$ bond energy like atoms covalent bond
- (4) The heat enthalpy change in a chemical reaction is equal but opposite to the heat enthalpy if reaction is reversed.
- (5) Hess's law can be verified experimentally.

(A) 1, 2, 3, 4

(B) 1, 2, 3, 4, 5

(C) 2, 3, 4, 5

(D) 3, 4, 5

Sol.

25. Heat of dissociation of CH_4 and C_2H_6 are 360 and 620 kcal mol^{-1} . The C - C bond energy would be :

(A) 60 kcal (B) 80 kcal (C) 100 kcal (D) 40 kcal

Sol.

26. If $C + \frac{1}{2} O_2 \rightarrow CO_{(g)}$; $\Delta H = - 110$ kJ.

$C + H_2O_{(g)} \rightarrow CO_{(g)} + H_2(g)$; $\Delta H = 132$ kJ The mole composition of mixture of steam and O_2 and steam on being passed over coke at 1273 K so that temperature remains constant is :

(A) 0.6 : 1 (B) 1.67 : 1 (C) 0.3 : 1 (D) 0.4 : 1

Sol.

27. The heat of fusion for water is +1.44 kcal. The heat required to change 27 g ice at $0^\circ C$ to water is :

(A) 2.16 kcal

(B) 0.72 kcal

(C) 25.92 kcal

(D) 2.88 kcal

Sol.

EXERCISE – III**SUBJECTIVE PROBLEMS (JEE ADVANCED)****Heat of reaction & it's type**

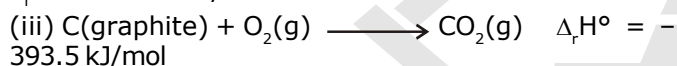
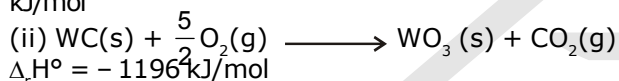
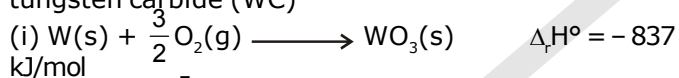
1. For urea $\text{NH}_2\text{CONH}_2(\text{S})$; $\Delta_f H^\circ_{298} = -333.5 \text{ kJ/mol}$.
Find $\Delta_f U^\circ_{298}$ of urea.

Sol.

Sol.

2. On the basis of following data,

Evaluate the standard enthalpy of formation of tungsten carbide (WC)



Sol.

4. The standard heats of formation of $\text{CH}_4(\text{g})$, $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ are -76.2 , -398.8 , $-241.6 \text{ kJ mol}^{-1}$. Calculate amount of heat evolved by burning 1 m^3 of methane measured at 1 atm & 273 K .

Sol.

3. Calculate $\Delta_r H^\circ$ for $\text{Fe}_2\text{O}_3(\text{s}) + 3\text{CO}(\text{g}) \longrightarrow 2\text{Fe}(\text{s}) + 3\text{CO}_2(\text{g})$

Given : $\Delta_f H^\circ (\text{Fe}_2\text{O}_3) = -822.2 \text{ kJ/mol}$

$\Delta_f H^\circ (\text{CO}, \text{g}) = -110.5 \text{ kJ/mol}$, $\Delta_f H^\circ (\text{CO}_2, \text{g}) = -393.5 \text{ kJ/mol}$

5. A cylinder of gas supplied by a company contains 14 kg of butane. The heat of combustion of butane is 2658 kJ/mol . A normal family requires 20 MJ of energy per day for cooking. If the cylinder lasts for 26 days, what percentage of gas is wasted due to inefficient combustion.

Sol.

6. A cylinder of gas is assumed to contain 11.2 kg of butane. If a normal family needs 20,000 kJ of energy per day for cooking, how long will the cylinder last if the enthalpy of combustion, $\Delta H = -2658$ kJ/mole for butane.

Sol.

8. When 12.0 g of carbon reacted with oxygen to form CO & CO₂ at 25°C & constant pressure, 75.0 kcal of heat was liberated and no carbon remained. Calculate the mass of oxygen which reacted.

$\Delta H_f^0(\text{CO}_2) = -95 \text{ kcal mol}^{-1}$, $\Delta H_f^0(\text{CO}) = -24 \text{ kcal mol}^{-1}$.

Sol.

7. The molar enthalpy of vaporization of benzene at its boiling point (353 K) is 30.84 kJ mol⁻¹. What is the molar internal energy change? For how long would a 12 volt source need to supply a 0.5 A current in order to vaporise 7.8 g of the sample at its boiling point?

Sol.

9. The heat of reaction $\frac{1}{2}\text{H}_2(\text{g}) + \frac{1}{2}\text{Cl}_2(\text{g}) \longrightarrow \text{HCl}(\text{g})$ at 27° C is -22.1 k cal. Calculate the heat of reaction at 77°C. The molar heat capacities at constant pressure at 27° for hydrogen, chlorine & HCl are 6.82, 7.70 & 6.80 cal mol⁻¹ respectively.

Sol.

10. Calculate the enthalpy change when infinitely dilute solutions of CaCl_2 and Na_2CO_3 are mixed. ΔH_f° for $\text{Ca}^{2+}(\text{aq})$, $\text{CO}_3^{2-}(\text{aq})$ and $\text{CaCO}_3(\text{s})$ are -129.80 , -161.65 , $-288.5 \text{ kcal mol}^{-1}$ respectively.

Sol.

12. The heat of solution of anhydrous CuSO_4 is -15.9 kcal and that of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is 2.8 kcal . Calculate the heat of hydration of CuSO_4 .

Sol.

13. The standard enthalpy of neutralization of KOH with (a) HCN (b) HCl in dilute solution is $-2480 \text{ cal. geq}^{-1}$ and $-13.68 \text{ kcal geq}^{-1}$ respectively. Find the enthalpy of dissociation of HCN at the same temperature.

Sol.

11. The enthalpies of neutralization of NaOH & NH_4OH by HCl are -13680 calories and -12270 cal respectively. What would be the enthalpy change if one gram equivalent of NaOH is added to one gram equivalent of NH_4Cl in solution? Assume that NH_4OH and NaCl are quantitatively obtained.

Sol.

14. If the enthalpy of formation of $\text{HCl}(\text{g})$ and $\text{Cl}^-(\text{aq})$ are -92.3 kJ/mole and -167.44 kJ/mol , find the enthalpy of solution of hydrogen chloride gas.

Sol.

Calorimeter

15. 0.16 g of methane was subjected to combustion at 27° C in a bomb calorimeter. The temperature of calorimeter system (including water) was found to rise by 0.5°C. Calculate the heat of combustion of methane at (i) constant volume (ii) constant pressure. The thermal capacity of calorimeter system is 17.7 kJ K⁻¹ (R = 8.313 mol⁻¹K⁻¹)

Sol.

16. 1.00 / sample of a mixture of CH₄(g) & O₂(g) measured at 25° C & 740 torr was allowed to react at constant pressure in a calorimeter which together with its contents had a heat capacity of 1260 cal/K. The complete combustion of the methane to CO₂ & H₂O caused a temperature rise in the calorimeter of 0.667 K. What was the mole percent of CH₄ in the original mixture ? $\Delta H^\circ_{\text{comb}}(\text{CH}_4) = -215 \text{ kcal mol}^{-1}$.

Sol.

17. A quantity of 1.92 of methanol was burnt in a constant pressure calorimeter. The temperature of water increased by 4.2°C. If the quantity of water surrounding the inner vessel was 2000 ml and the heat capacity of the inner vessel was 2.02 kJ/°C. Calculate the heat of combustion of methanol. [Specific heat of capacity of H₂O = 4.18 J/g°C]

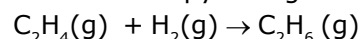
Sol.

Bond energy

18. The enthalpy of dissociation of PH₃ is 954 kJ/mol and that of P₂H₄ is 1.48 M J mol⁻¹. What is the bond enthalpy of the P – P bond ?

Sol.

19. Using the bond enthalpy data given below, calculate the enthalpy change for the reaction.



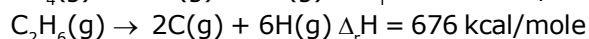
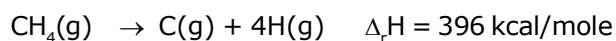
Data :

Bond	C – C	C = C	C – H	H – H
Bond Enthalpy	336.81 kJ/mol	606.68 kJ/mol	410.87 kJ/mol	431.79 kJ/mol

Sol.

Sol.

20. The enthalpy change for the following process at 25°C and under constant pressure at 1 atm are as follows :



Calculate C – C bond energy in C_2H_6 & heat of formation of C_2H_6 (g)

Given : $\Delta_{\text{sub}} \text{C}(\text{s}) = 171.8 \text{ kcal/mole}$

B.E. (H – H) = 104.1 kcal/mole

Sol.

22. From the following data : Enthalpy of formation of $\text{CH}_3\text{CN} = 87.86 \text{ kJ/mol}$, Enthalpy of formation of $\text{C}_2\text{H}_6 = -83.68 \text{ kJ/mol}$

Enthalpy of sublimation of graphite = 719.65 kJ/mol

Enthalpy of dissociation of nitrogen = 945.58 kJ/mol;

Enthalpy of dissociation of $\text{H}_2 = 435.14 \text{ kJ/mol}$

C – H bond enthalpy = 414.22 kJ/mol

Calculate the (i) $\epsilon_{\text{C-C}}$; (ii) $\epsilon_{\text{C}\equiv\text{N}}$

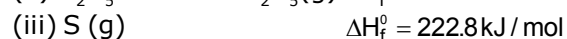
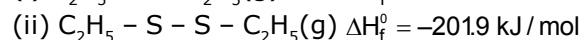
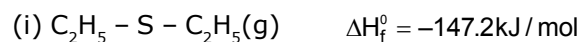
Sol.

21. The polymersiation of ethylene to linear polyethylene is represented by the reaction $n\text{CH}_2 = \text{CH}_2 \rightarrow (-\text{CH}_2 - \text{CH}_2)_n$ where n has a large integral value. Given that the average enthalpies of bond dissociation for C = C & C – C at 298 K are +590 & +331 kJ mol⁻¹ respectively. Calculate the enthalpy of polymerisation per mole of ethylene at 298 K.

23. The heat of combustion of acetylene is 312 kcal. If heat of formation of CO_2 & H_2O are -94.38 & -68.38 kcal respectively, calculate $\text{C} \equiv \text{C}$ bond energy. Given that heat of atomisation of C is 150 kcal and H – H bond energy and C – H bond energy are 103 kcal and 93.64 kcal respectively.

Sol.

25. Find the enthalpy of S – S bond from the following data.



Sol.

24. Using the given data calculate enthalpy of formation of acetone (g). [All values in kJ mol^{-1}]
bonding energy of ; C – H = 413.4 ; C – C = 347.0 ;
C = O = 728.0 ; O = O = 495.0 ; H – H = 435.8
; ΔH_{sub} of C = 718.4

Sol.

Resonance Energy

26. The enthalpy of formation of ethane, ethylene and benzene from the gaseous atoms are -2839.2 , -2275.2 and $-5506 \text{ kJ mol}^{-1}$ respectively. Calculate the resonance energy of benzene. The bond enthalpy of C – H bond is given as equal to $+410.87 \text{ kJ/mol}$.

Sol.

27. Calculate the heat of combustion of methyl alcohol at 298 K from the following data

Bond C – H C – O O – H O = O C = O

Energy kJ mol⁻¹ 414 351.5 464.5 494 711

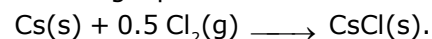
Resonance energy of CO₂ = -143 kJ mol⁻¹

Latent heat of vaporisation of methyl alcohol = 35.5 kJ mol⁻¹

Latent heat of vaporisation of water = 40.6 kJ mol⁻¹.

Sol.

29. Cesium chloride is formed according to the following equation



The enthalpy of sublimation of Cs, enthalpy of dissociation of chlorine, ionization energy of Cs & electron gain enthalpy of chlorine are 81.2, 243.0, 375.7 and -348.3 kJ mol⁻¹. The energy change involved in the formation of CsCl is -388.6 kJ mol⁻¹. Calculate the lattice energy of CsCl.

Sol.

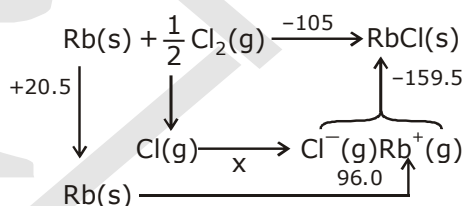
Born Haber cycle

28. Calculate the electron gain enthalpy of fluorine atom using the following data. Make Born - Haber's cycle. All the values are in kJ mol⁻¹ at 25°C. $\Delta H_{\text{diss}}(\text{F}_2) = 160$, $\Delta H_f^\circ(\text{NaF(s)}) = -571$, I.E.

$[\text{Na(g)}] = 494$, $\Delta H_{\text{vap}}[\text{Na(s)}] = 101$. Lattice energy of NaF(s) = -894.

Sol.

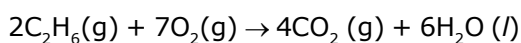
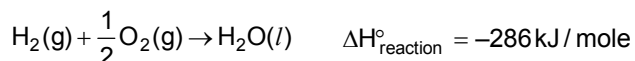
30. The Born-Haber cycle for rubidium chloride (RbCl) is given below (the energies are in kcal mol⁻¹)



Find the value of X.

Sol.

31. From the following data,
 $\text{C(s, graphite)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$



$$\Delta H^\circ_{\text{reaction}} = -3120 \text{ kJ/mole}$$

Calculate the standard enthalpy of formation of $\text{C}_2\text{H}_6(\text{g})$ (in kJ/mole)

Sol.

32. Calculate the mass of mercury which can be liberated from HgO at 25°C by the treatment of excess HgO with 41.84 kJ of heat at

(a) constant pressure (b) constant volume conditions

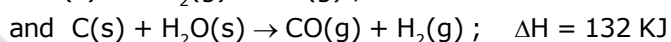
Given : $\Delta H^\circ_f(\text{HgO, s}) = -90.8 \text{ kJ mol}^{-1}$ & $M(\text{Hg}) = 200.6 \text{ g mol}^{-1}$.

Sol.

33. For reduction of ferric oxide by hydrogen,
 $\text{Fe}_2\text{O}_3(\text{s}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{Fe}(\text{s}) + 3\text{H}_2\text{O}(\text{l})$; $\Delta H^\circ_{298} = -35.1 \text{ kJ}$. The reaction was found to be too exothermic to be convenient. It is desirable that ΔH° should be at the most -26 kJ . At what temperature is it possible ?
 $C_p[\text{Fe}_2\text{O}_3] = 104.5$, $C_p[\text{Fe}(\text{s})] = 25.5$, $C_p[\text{H}_2\text{O}(\text{l})] = 75.3$,
 $C_p[\text{H}_2(\text{g})] = 28.9$
 (all in J/mol)

Sol.

34. From the following data of ΔH of the following reactions



Calculate the mole composition of the mixture of steam and oxygen on being passed over coke at 1273 K , keeping the reaction temperature constant.

Sol.

35. Although C_p is usually assumed to be constant, for more accurate calculations we must consider its variation with temperature as well. This relation is given by :

$$C_p = a + bT + cT^2 + dT^3 \text{ mol}^{-1} \text{ K}^{-1}$$

(a) Find the expression for the amount of heat required to raise the temperature of 1 mole of gas from $T_1 \text{ K}$ to $T_2 \text{ K}$, while

(i) keeping the first term [i.e. $C_p = a$](ii) keeping the first two terms.

(ii) keeping all the terms of the above expression. Note that each successive term introduces higher accuracy.

(b) For CO_2 , $a = 5.0$, $b = 15 \times 10^{-5}$. Find the heat required (for one mole) to raise its temperature from 300 K to 500 K in case (i) and case (ii). Case (ii) gives a more accurate value. Find the percent error in case (i).

Sol.

36. An intimate mix of ferric oxide & Al is used as solid rocket fuel. Calculate the fuel value per gm & fuel value per CC of the mixture. Heats of formation & densities are :

$\Delta H_f^\circ (\text{Al}_2\text{O}_3) = -399 \text{ k cal/mole}$; $\Delta H_f^\circ (\text{Fe}_2\text{O}_3) = -199 \text{ kcal/mole}$,

density of $\text{Fe}_2\text{O}_3 = 5.2 \text{ g/cc}$; density of Al = 2.7 g/cc .

Sol.

37. A person takes 15 breaths per minute. The volume of air inhaled in each breath is 448 ml and contains 21% of oxygen by volume. The exhaled air contains 16% of oxygen by volume. If all the oxygen is used in the combustion of sucrose, how much of the latter is burnt in the body per day & how much heat is evolved. ΔH_{com} of sucrose is $= -6000 \text{ kJ mol}^{-1}$. Take temperature to be 300 K throughout.

Sol.

38. The enthalpies of neutralization of weak acid HA & a weak acid HB by NaOH are $-6900 \text{ cal/equivalent}$ & $-2900 \text{ cal/equivalent}$ & $-2900 \text{ cal/equivalent}$ respectively. When one equivalent of NaOH is added to a solution containing one equivalent of HA & one equivalent of HB, the enthalpy change was -3900 calories . In what ratio is the base distributed between HA & HB ?

Sol.

39. Calculate the heat produced when 3.785 litre of octane (C_8H_{18}) reacts with oxygen to form CO & water vapour at $25^\circ C$. The density of octane is 0.7025 gm/ml . Heat of combustion of C_8H_{18} is -1302.7 kcal/mol .

$$\Delta H_f^\circ CO_2(g) = -94.05 \text{ kcal mol}^{-1}; \Delta H_f^\circ CO(g) = -26.41 \text{ kcal mol}^{-1}$$

$$\Delta H_f^\circ H_2O(l) = -68.32 \text{ kcal mol}^{-1}; \Delta H_f^\circ H_2O(g) = -57.79 \text{ kcal mol}^{-1}$$

Sol.

40. Using the data (all values are in kJ/mole at $25^\circ C$) given below

$$\Delta H_{\text{combustion}}^\circ (\text{ethane}) = -1559.8; \Delta H_{\text{combustion}}^\circ (\text{ethene}) = -1410.9$$

$$\Delta H_{\text{combustion}}^\circ (\text{acetylene}) = -1299.7; \Delta H_{\text{combustion}}^\circ (\text{acetaldehyde}) = -1192.3$$

$$\Delta H_f^\circ CO_2(g) = -393.5; \Delta H_f^\circ H_2O(l) = -285.8$$

$$\Delta H^\circ \text{ for } C_{(s)} (\text{graphite}) \rightarrow C_{(g)} = +716.68;$$

$$\text{Bond energy of } H-H = 435.94$$

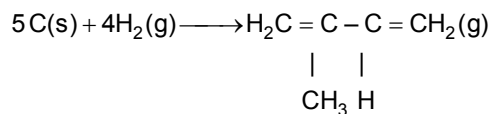
$$\text{Bond energy of } O=O = 498.94$$

Calculating the following bond energies :

$$(i) C-C (ii) C-H (iii) C=O (iv) C=C (v) C \equiv C$$

Sol.

41. Using bond energy data, calculate heat of formation of isoprene.



$$\text{Given : } C-H = 98.8 \text{ kcal ; } H-H = 104 \text{ kcal ;}$$

$$C-C = 83 \text{ kcal ; } C=C = 147 \text{ kcal \&}$$

$$C(s) \rightarrow C(g) = 171 \text{ kcal.}$$

Sol.

42. Compute the heat of formation of liquid methyl alcohol in kJ mol^{-1} , using the following data. Heat of vaporisation of liquid $CH_3OH = 38 \text{ kJ/mol}$. Heat of formation of gaseous atoms from the elements in their standard states ; H, 218 kJ/mol ; C, 715 kJ/mol ; O, 249 kJ/mol Average Bond energies C-H, 415 kJ/mol ; C-O, 356 kJ/mol ; O-H, 463 kJ/mol

Sol.

43. Calculate the enthalpy change for the reaction $\text{XeF}_4 \rightarrow \text{Xe}^+ + \text{F}^- + \text{F}_2 + \text{F}$. The average Xe – F bond energy is 34 kcal/mol, first I.E. of Xe is 279 kcal/mol, electron affinity of F is 85 kcal/mol & bond dissociation energy of F_2 is 38 kcal/mol.

Sol.

44. By using the following data draw an appropriate energy cycle & calculate the enthalpy change of hydration of (i) the chloride ion ; (ii) the iodide ion. comment on the difference in their values.

- enthalpy change of solution of $\text{NaCl(s)} = -2 \text{ kJ/mol}$
- enthalpy change of solution of $\text{NaI(s)} = +2 \text{ kJ/mol}$
- enthalpy change of hydration of $\text{Na}^+(\text{g}) = -390 \text{ kJ/mol}$
- lattice energy of $\text{NaCl} = -772 \text{ kJ/mol}$
- lattice energy of $\text{NaI} = -699 \text{ kJ/mol}$.

Sol.

45. The standard enthalpy of combustion of sucrose is $-5645 \text{ kJ mol}^{-1}$. What is the advantage (in kJ mol^{-1} of energy released as heat) of complete aerobic oxidation compared to anaerobic hydrolysis of sucrose to lactic acid ? ΔH_f° for lactic acid, CO_2 and H_2O is -694 , -395.0 and -286.0 respectively

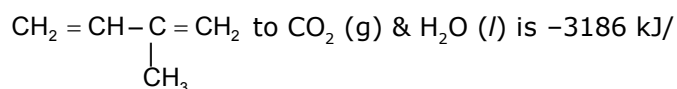
Sol.

46. Calculate the proton gain enthalpy of $\text{NH}_3(\text{g})$ from the following data (in kJ/mole)

$\Delta H_{\text{dissociation}}^\circ : \text{H}_2(\text{g}) = 218 ; \Delta H_{\text{dissociation}}^\circ : \text{Cl}_2(\text{g}) = 124$
 $\Delta H_{\text{formation}}^\circ : \text{NH}_3(\text{g}) = -46 ; \Delta H_f^\circ : \text{NH}_4\text{Cl(s)} = -314$
Lattice energy of $\text{NH}_4\text{Cl(s)} = -683$
Ionization energy of $\text{H} = 1310$
Electron affinity of $\text{Cl} = 348$

Sol.

47. Heat of combustion of gaseous isoprene (C_5H_8)



mole.

Calculate the heat of formation and compare with bond energies. Calculate the resonance energy of isoprene.

Given : $\Delta_f H (CO_2, g) = -393.5 \text{ kJ/mol}$; $\Delta_f H (H_2O, l) = -285.84 \text{ kJ/mol}$

Bond energies of C – H, C – C & C = C are 413, 348 and 615 kJ.

Heat of atomization of carbon and H_2 are 718.4 and 435.8

Sol.

48. The enthalpy of formation of $C_2H_5OH(l)$ is -66 kcal/mol . The enthalpy of combustion of $CH_3 - O - CH_3$ is -348 kcal/mol . Given that the enthalpies of formation of $CO_2(g)$ and $H_2O(l)$ are -94 kcal/mol & -68 kcal/mol respectively, calculate ΔH for the isomerisation of ethanol to methoxymethane. All data are at $25^\circ C$.

Sol.

49. What is the ratio of the energy yield on combustion of hydrogen atoms to steam to the yield on combustion of an equal mass of hydrogen molecules to steam ?

Given ; $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$; $\Delta H = -242 \text{ kJ}$

B.E. (H – H) = 436 kJ

Sol.

50. Fe_xO_4 a mixed oxide of iron consists of only Fe^{+2} & Fe^{+3} ions, with the ratio of $Fe^{+2} : Fe^{+3} = 1 : 2$ in the mixed oxide. From the data given below,

Enthalpy of formation, $\Delta_f H (Fe_xO_4) = -1092 \text{ kJ/mol}$.

Enthalpy of sublimation. $\Delta_{sub} H (Fe) = 390 \text{ kJ/mol}$

B.D.E of $O_2 = 490 \text{ kJ/mol}$

I.E₁ of Fe = 760 kJ/mol

I.E₂ of Fe = 1560 kJ/mol

I.E₃ of Fe = 2960 kJ/mol

I.E₁ of $O^{2-} = -844 \text{ kJ/mol}$

I.E₂ of $O^{2-} = 142 \text{ kJ/mol}$.

Lattice Energy of $Fe_xO_4 = 18930 \text{ kJ/mol}$.

Prove that value of x is 3 with the help of given data.

Sol.

EXERCISE – IV**PREVIOUS YEARS PROBLEMS****LEVEL – I****JEE MAIN**

1. If at 298 K the bond energies of C–H, C–C, C=C and H–H bonds are respectively 414, 347, 615 and 435 kJ mol⁻¹, the value of enthalpy change for the reaction ;
 $\text{H}_2\text{C}=\text{CH}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{H}_3\text{C}-\text{CH}_3(\text{g})$ at 298 K will be – **[AIEEE-2003]**
 (A) +125 kJ (B) –125 kJ
 (C) +250 kJ (D) – 250 kJ

Sol.

2. The enthalpy change for a reaction does not depend upon – **[AIEEE-2003]**
 (A) The nature of intermediate reaction steps
 (B) The differences in initial or final temperatures of involved substances
 (C) The physical states of reactants and products
 (D) Use of different reactants for the same product

Sol.

3. The enthalpies of combustion of carbon and carbon monoxide are – 393.5 and – 283 kJ mol⁻¹ respectively. The enthalpy of formation of carbon monoxide per mole – **[AIEEE-2004]**
 (A) 110.5 kJ (B) 676.5 kJ
 (C) – 676.5 kJ (D) – 110.5 kJ

Sol.

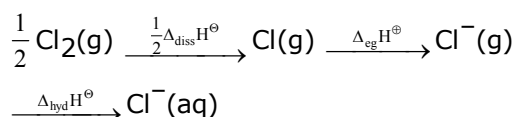
4. If the bond dissociation energies of XY, X₂ and Y₂ (all diatomic molecules) are in the ratio of 1 : 1 : 0.5 and Δ_fH for the formation of XY is – 200 kJ mol⁻¹. The bond dissociation energy of X₂ will be – **[AIEEE-2005]**
 (A) 200 kJ mol⁻¹ (B) 100 kJ mol⁻¹
 (C) 800 kJ mol⁻¹ (D) 300 kJ mol⁻¹

Sol.

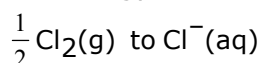
5. The standard enthalpy of formation (Δ_fH°) at 298 K for methane, CH₄(g), is –74.8 kJ mol⁻¹. The additional information required to determine the average energy for C – H bond formation would be – **[AIEEE 2006]**
 (A) latent heat of vaporization of methane
 (B) the first four ionization energies of carbon and electron gain enthalpy of hydrogen
 (C) the dissociation energy of hydrogen molecule H₂
 (D) The dissociation energy of H₂ and enthalpy of sublimation of carbon

Sol.

6. Oxidising power of chlorine in aqueous solution can be determined by the parameters indicated below :



The energy involved in the conversion of

(using the data, Δ_{diss} H_{Cl₂} = 240 kJ mol⁻¹,Δ_{eg} H_{Cl} = –349 kJ mol⁻¹, Δ_{hyd} H_{Cl⁻} = –381

kJ mol^{-1}) will be - [AIEEE 2008]
 (A) -610 kJ mol^{-1} (B) -850 kJ mol^{-1}
 (C) $+120 \text{ kJ mol}^{-1}$ (D) $+152 \text{ kJ mol}^{-1}$

Sol.

7. On the basis of the following thermochemical data $(\Delta H_f^\circ)_{\text{H}^+} = 0$
 $\text{H}_2\text{O}(l) \longrightarrow \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}); \Delta H = 57.32 \text{ kJ}$
 $\text{H}_2(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(l); \Delta H = -286.20 \text{ kJ}$
 The value of enthalpy of formation of OH^- ion at 25°C is - [AIEEE 2009]
 (A) -228.88 kJ (B) $+228.88 \text{ kJ}$
 (C) -343.52 kJ (D) -22.88 kJ

Sol.

8. In a fuel cell methanol is used as fuel and oxygen gas is used as an oxidizer. The reaction is
 $\text{CH}_3\text{OH}(l) + \frac{3}{2} \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(l)$
 At 298 K standard Gibbs energies of formation for $\text{CH}_3\text{OH}(l)$, $\text{H}_2\text{O}(l)$ and $\text{CO}_2(\text{g})$ are -166.2 , -237.2 and $-394.4 \text{ kJ mol}^{-1}$ respectively. If standard enthalpy of combustion of methanol is -726 kJ mol^{-1} , efficiency of the fuel cell will be - [AIEEE 2009]
 (A) 87% (B) 90%
 (C) 97% (D) 80%

Sol.

9. The standard enthalpy of formation of NH_3 is $-46.0 \text{ kJ mol}^{-1}$. If the enthalpy of formation of H_2 from its atoms is -436 kJ mol^{-1} and that of N_2 is -712 kJ mol^{-1} , the average bond enthalpy of $\text{N}-\text{H}$ bond in NH_3 is

[AIEEE 2010]

- (A) $-1102 \text{ kJ mol}^{-1}$ (B) -964 kJ mol^{-1}
 (C) $+352 \text{ kJ mol}^{-1}$ (D) $+1056 \text{ kJ mol}^{-1}$

Sol.

10. The value of enthalpy change (ΔH) for the reaction [AIEEE 2011]
 $\text{C}_2\text{H}_5\text{OH}_{(l)} + 3\text{O}_{2(g)} \rightarrow 2\text{CO}_{2(g)} + 3\text{H}_2\text{O}_{(l)}$
 at 27°C is $-1366.5 \text{ kJ mol}^{-1}$. The value of internal energy change for the above reaction at this temperature will be -
 (A) -1369.0 kJ (B) -1364.0 kJ
 (C) -1361.5 kJ (D) -1371.5 kJ

Sol.

11. Consider the reaction :
 $4\text{NO}_{2(g)} + \text{O}_{2(g)} \rightarrow 2\text{N}_2\text{O}_{5(g)}; \Delta_r H = -111 \text{ kJ}$
 If $\text{N}_2\text{O}_{5(s)}$ is formed instead of $\text{N}_2\text{O}_{5(g)}$ in the above reaction, the $\Delta_r H$ value will be : (given, ΔH of sublimation for N_2O_5 is 54 kJ mol^{-1}) [AIEEE 2011]
 (A) $+54 \text{ kJ}$ (B) $+219 \text{ kJ}$
 (C) -219 kJ (D) -165 kJ

Sol.

12. In view of the signs of $\Delta_r G^\circ$ for the following reactions :
 $\text{PbO}_2 + \text{Pb} \rightarrow 2 \text{PbO}, \Delta_r G^\circ < 0$
 $\text{SnO}_2 + \text{Sn} \rightarrow 2 \text{SnO}, \Delta_r G^\circ > 0$,
 which oxidation states are more characteristic for lead and tin ? [AIEEE 2011]
 (A) For lead + 2, for tin + 2
 (B) For lead + 4, for tin + 4
 (C) For lead + 2, for tin + 4
 (D) For lead + 4, for tin + 2

Sol.

LEVEL – II

JEE ADVANCED

OBJECTIVE

1. Which of the following is not an endothermic reaction ?

(A) Combustion of methane
 (B) Decomposition of water
 (C) Dehydrogenation of ethene to ethylene
 (D) Conversion of graphite to diamond

[JEE 1999]

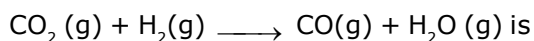
Sol.

2. Estimate the average S – F bond energy in SF_6 . The ΔH_f° values of $\text{SF}_6(\text{g})$, $\text{S}(\text{g})$, and $\text{F}(\text{g})$ are -1100 , 275 and 80 kJ/mol respectively.

[JEE 1999]

Sol.

3. ΔH_f° for $\text{CO}_2(\text{g})$, $\text{CO}(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ are -393.5 , -110.5 and -241.8 kJ mol $^{-1}$ respectively. The standard enthalpy change (in kJ) for the reaction

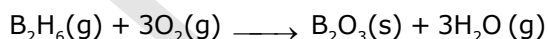


(A) 524.1 (B) 41.2
 (C) -262.5 (D) -41.2

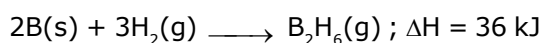
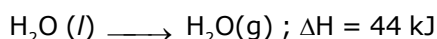
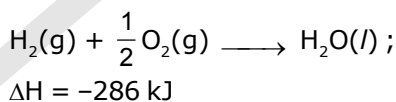
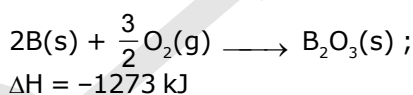
[JEE 2000]

Sol.

4. Diborane is potential rocket fuel which undergoes combustion according to the reaction,



From the following data, calculate the enthalpy change for the combustion of diborane :



[JEE 2000]

Sol.

5. Which of the following reactions defines ΔH_f° ?

- (A) $C_{(\text{diamond})} + O_2(g) \rightarrow CO_2(g)$
 (B) $\frac{1}{2} H_2(g) + \frac{1}{2} F_2(g) \rightarrow HF(g)$
 (C) $N_2(g) + 3H_2(g) \rightarrow 2NH_3$
 (D) $CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$

[JEE 2003]

Sol.

6. In a constant volume calorimeter, 3.5 g of a gas with molecular weight 28 was burnt in excess oxygen at 298.0 K. The temperature of the calorimeter was found to increase from 298.0 K to 298.43 K due to the combustion process. Given that the heat capacity of the calorimeter is 2.5 kJ K^{-1} , the numerical value for the enthalpy of combustion of the gas in kJ mol^{-1} is

[JEE 2009]

Sol.

7. The bond energy (in kcal mol^{-1}) of a C-C single bond is approximately

[JEE 2010]

- (A) 1 (B) 10 (C) 100 (D) 1000

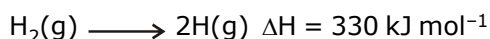
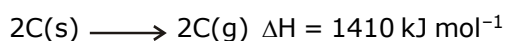
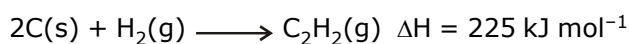
Sol.

8. The species which by definition has zero standard molar enthalpy of formation at 298 K is [JEE 2010]

- (A) $Br_2(g)$ (B) $Cl_2(g)$ (C) $H_2O(g)$ (D) $CH_4(g)$

Sol.

9. Using the data provided, calculate the multiple bond energy (kJ mol^{-1}) of a $C \equiv C$ bond in C_2H_2 . That energy is (take the bond energy of a C-H bond as 350 kJ mol^{-1})



- (A) 1165 (B) 837 (C) 865 (D) 815

[JEE 2012]

Sol.

10. The standard enthalpies of formation of $CO_2(g)$, $H_2O(l)$ and glucose(s) at 25°C are -400 kJ/mol , -300 kJ/mol and -1300 kJ/mol , respectively. The standard enthalpy of combustion per gram of glucose at 25°C is

- (A) $+2900 \text{ kJ}$ (B) -2900 kJ
 (C) -16.11 kJ (D) $+16.11 \text{ kJ}$

Sol.

[JEE Advance 2013]

Answers

Answer Ex-I

OBJECTIVE PROBLEMS (JEE MAIN)

1. D 2. D 3. D 4. A 5. C 6. C 7. B 8. A
9. A 10. C 11. A 12. D 13. D 14. C
15. A 16. B 17. B 18. B 19. B 20. C 21. B 22. B
23. D 24. B 25. C 26. C 27. A 28. A 29. D 30. B
31. B 32. D 33. B 34. C 35. B 36. A 37. C 38. C
39. C 40. D 41. D 42. (i) B (ii) A (iii) A (iv) C 43. A 44. B 45. B
46. A 47. B 48. B 49. A 50. A

Answer Ex-II

OBJECTIVE PROBLEMS (JEE ADVANCED)

1. C,D 2. A,B,C 3. C,D 4. A,B,C 5. B,C,D 6. A,Ca 7. C,D 8. B,C,D
9. A,B,C 10. A,C 11. A,C,D 12. A,B,C,D 13. A,C,D
14. $A \rightarrow (P,R)$, $B \rightarrow (Q,S)$, $C \rightarrow (Q,S)$, $D \rightarrow (Q,S)$
15. $A \rightarrow (P,S)$, $B \rightarrow (Q)$, $C \rightarrow (R)$ 16. A 17. B 18. B 19. A 20. A
21. A 22. D 23. B 24. A 25. B 26. B 27. A

Answer Ex-III**SUBJECTIVE PROBLEMS (JEE ADVANCED)**

1. -324.8 kJ/mol 2. -34.5 kJ/mol 3. -26.8 kJ/mol 4. 35.973 MJ
5. 18.95% 6. 25.66 days 7. $\Delta E = 27.91 \text{ KJ mol}^{-1}$, $t = 514 \text{ sec.}$
8. 27.43 g O_2 9. -22.123 k cal 10. 2.95 kcal 11. -1410 cal 12. -18.7 kcal
13. 11.2 Kcal 14. -75.14 kJ/mol 15. (i) -885 kJ/mol (ii) -889.980 kJ/mol
16. 10.0 mol\% CH_4 17. -726.6 kJ/mol 18. 208 kJ/mol 19. -120.08 J/ml
20. B.E. (C – C) = 82 kcal/mole ; $\Delta_f H [\text{C}_2\text{H}_6(\text{g})] = -20.1 \text{ kcal/mole}$ 21. -72 kJmol^{-1}
22. (i) 343.08 ; (ii) 891.2 23. $E_{\text{C}=\text{C}} = 160.86 \text{ k cal}$ 24. $-192.3 \text{ kJ mol}^{-1}$ 25. 277.5 kJ/mol
26. -23.68 KJ/mol 27. -669.7 kJ mol 28. -352 kJ mol^{-1} 29. $-618.7 \text{ kJ mol}^{-1}$ 30. $-90.75 \text{ kcal mol}^{-1}$
31. -85 kJ/mole 32. (a) 92.435 g (b) 93.72 g 33. 404 K
34. mole % $\text{O}_2(\text{g}) = 37.5$, $\text{H}_2\text{O}(\text{g}) = 62.5$
35. (a) (i) $a\Delta T$ (ii) $a\Delta T + \frac{b}{2}(T_2^2 - T_1^2)$ (b) 1000cal , 1012cal , 1.1858% error
36. $0.9346 \text{ k cal g}^{-1}$, $3.94 \text{ kcal cm}^{-3}$ 37. $9.822 \text{ MJ/day evolved}$
38. $1 : 3$ 39. $-666.81 \text{ k cal mol}^{-1}$, 15.55 Mcal
40. C – C = 97.81 kJ , C – H = 454.64 kJ , C = O = 804.26 kJ , C = C = 434.3 kJ , C = C = 733.48 kJ
41. $+20.6 \text{ kcal}$ 42. -266 kJ mol^{-1} 43. 292 kcal/mol
44. for Cl– 384 kJ mol^{-1} , for I– 307 kJ mol^{-1} 45. advantage = 5393 kJ mol^{-1}
46. -718 kJ/mol 47. -30.06 kJ/mol 48. 22 kcal mol^{-1}
49. $2.80 : 1$

Answer Ex-IV**PREVIOUS YEARS PROBLEMS****LEVEL – I****JEE MAIN**

1. B 2. A 3. D 4. C 5. D
6. A 7. A 8. C 9. C 10. B
11. C 12. C

LEVEL – II**JEE ADVANCED**

1. A 2. 309.6 kJ/mol 3. B 4. $-2035 \text{ kJ mol}^{-1}$ 5. B 6. 9
7. C 8. B 9. D 10. C